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Organic Reagents[1] in Qualitative Analysis. I. The Separation of Iron, Chromium and Aluminum

BY LEO LEHRMAN, ELVIN A. KABAT AND HAROLD WEISBERG

In the usual methods of analysis of the ammonium sulfide group a mixture of sodium hydroxide and sodium peroxide is employed to separate the iron and aluminum groups.[2,3] It is a well known fact that these reagents, especially the former, due to its action on glass, introduce small amounts of aluminum and silica into the solution.[4,5] In the final precipitation of aluminum ion by ammonium hydroxide any silica originally present will also be precipitated as silicic acid. This precipitate may be mistaken for aluminum hydroxide, though the use of aluminon will overcome this possible error.[6] However, it would be preferable to separate and detect aluminum ion without the use of sodium hydroxide and sodium peroxide or at least before they are added.

The problem would be simplified considerably if it were possible to separate the trivalent from the divalent metallic ions. Ammonium hydroxide in the presence of ammonium salts has been shown to be unreliable[7] even when the P_H of the solution has been controlled.[8] Recently the separation of ferric ion from the divalent metallic ions was reported by using hexamethylenetetramine which, it is stated, acts as a very weak base in acid solution and precipitates ferric hydroxide.[9] The authors claim that from a study of the P_H's at which chromic hydroxide and the hydroxides of the divalent metallic ions form, it would be impossible to make a separation. However, experimentation sho[illegible] [illegible] of each metallic ion containing a[illegible] trivalent [illegible] are precipitated by hexamethylenetetramine. This fact suggested a possible method of separation when the metallic ions are present together. Further work confirmed this possibility.

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[1] The organic reagents are made by [illegible]

[2] Noyes, "Qualitative Chemical Ana[illegible]

[3] Curtman, "Qualitative Chemical A[illegible]

[4] Ref. (1), p. 99, Note [illegible]

[5] Ref. (2), p. 327, Note 21.

[6] Hammett and Sottery, THIS JOURNAL, 47, 142 (1925).

[7] Noyes, Bray and Spear, *ibid.*, 30, 482, Notes 2, 3, 4, 5, 495–499 (1908); W. D. Treadwell, *Schweiz. Chem.-Ztg.*, 2, 59 (1918).

[8] Swift and Barton, THIS JOURNAL, 54, 2219 (1932).

[9] Ray and Chattopadaya, *Z. anorg. allgem. Chem.*, 169, 99–112 (1928).

Experimental

Reactions of the Metallic Ions with Hexamethylenetetramine.—To 100 mg. separately of each of the metallic ions in 10 cc. of solution, excess 10% $(CH_2)_6N_4$ in water solution was added. If precipitation took place the reagent was added until complete and the mixture filtered. To both the filtrates and the solutions in which there was no precipitation, concentrated ammonia was added to distinct alkalinity and then hydrogen sulfide passed in. The experiments were repeated only boiling after the addition of $(CH_2)_6N_4$ and in a third group 1 g. ammonium nitrate was added first. Table I shows the results of these experiments.

TABLE I

REACTIONS OF METALLIC IONS WITH $(CH_2)_6N_4$

Metallic ion	$(CH_2)_6N_4$, precipitation	$(CH_2)_6N_4$ + boiling, precipitation	1 g. NH_4NO_3 + $(CH_2)_6N_4$, precipitation	1 g. NH_4NO_3 + $(CH_2)_6N_4$ + boiling, precipitation
Fe^{+++}	Complete	Complete	Complete	Complete
Al^{+++}	None	Complete	Complete	Complete
Cr^{+++}	None	Complete	None	Complete
Ni^{++}	None	Partial	None	None
Co^{++}	None	Partial	None	None
Mn^{++}	None	Partial	None	None
Zn^{++}	Partial	Complete	None	None
Fe^{++}	Partial	Partial	Partial	Partial

Separation of Trivalent Metallic Ions from Divalent.—To a mixture of 100 mg. of Fe^{++} and 5 mg. of Mn^{++} in a solution of 75 cc. of 0.3 *N* hydrochloric acid containing 1 g. of ammonium nitrate, comparable to the filtrate from the previous group after the hydrogen sulfide has been boiled out, 5 cc. of 3% hydrogen peroxide was added and boiled for five minutes in order to oxidize the Fe^{++} to Fe^{+++}; 10% $(CH_2)_6N_4$ solution was then added to the boiling solution until no more precipitation took place. The filtrate was concentrated to 20 cc. and divided in half. Both solutions were treated with ammonium sulfide, the precipitates filtered and washed. One precipitate was tested for Mn^{++} by the sodium bismuthate method and the other by a sodium carbonate bead and potassium chlorate. Both methods gave positive results. The experiment was repeated using 100 mg. of each of the other trivalent metallic ions separately and 5 mg. of Mn^{++}. Positive tests for Mn^{++} were obtained. Further experiments showed that 1 mg. of Mn^{++} originally in the presence of 100 mg. of each of the trivalent metallic ions together could be detected by the sodium bismuthate method and 2 mg. by the bead test. A solution of 100 mg. of each of the trivalent metallic ions together was carried through the same procedure. The filtrate after the addition of $(CH_2)_6N_4$ yielded no precipitate with ammonium sulfide, showing complete precipitation by $(CH_2)_6N_4$.

The above experiments were repeated using Zn^{++} instead of Mn^{++}. The filtrates from the $(CH_2)_6N_4$ precipitation were evaporated to 10 cc., cooled, filtered if salts crystallized out, and the filtrates tested for Zn^{++} with freshly prepared potassium ferrocyanide solution. The results showed that 1 mg. of Zn^{++} originally in the presence of 100 mg. of each of the trivalent metallic ions together could be detected.

The same experiments were carried out separately with Ni^{++} and Co^{++} and gave similar results, the Ni^{++} being detected with dimethylglyoxime and the Co^{++} by α-nitroso-β-naphthol.

A solution containing 100 mg. each of the trivalent metallic ions, 2 mg. of Mn^{++} and 1 mg. each of the other divalent metallic ions was used in the next experiment. The filtrate from the $(CH_2)_6N_4$ precipitation was analyzed for each divalent metallic ion, positive tests resulting.

Before the procedure could be tried to find out if small amounts of the trivalent metallic ions in the presence of large amounts of the divalent could be separated, an adequate method of detecting the trivalent metallic ions when together was necessary. The method finally developed precipitates Fe^{+++} with cupferron,[10] oxidizes Cr^{+++} to $CrO_4^{=}$ with ammonium persulfate in the presence of silver ion[11,12] and detects Al^{+++} in a weakly acid solution with $(CH_2)_6N_4$. Experiments showed that 1 mg. of each of the trivalent metallic ions together in the presence of 100 mg. of each of the divalent together were effectively separated and detected. Furthermore, it was shown that 1 mg. of each trivalent metallic ion in the presence of 100 mg. of each of the other metallic ions of this group together could be separated and detected.

In order to determine whether or not any Al^{+++} is introduced from the metallic ions of previous groups, a 50-cc. solution containing 100 mg. of each of these metallic ions was made. The silver group was precipitated with Cl^- and filtered, the Cl^- in the filtrate removed by evaporation with HNO_3[13] and after adjustment of the acidity to 0.3 N hydrochloric acid completely precipitated with hydrogen sulfide. The filtrate, after removal of the hydrogen sulfide, was concentrated and divided into three portions. One portion was treated with ammonium hydroxide, the second with ammonium sulfide and the third with $(CH_2)_6N_4$ and boiled. No precipitate formed in any case, showing that no Al^{+++} had been introduced.

Summary

1. The reactions of the metallic ions of the ammonium sulfide group with hexamethylenetetramine under varying conditions have been investigated.

2. A separation of the trivalent from the divalent metallic ions, based on these reactions, has been effected.

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(10) Baudisch and King, *J. Ind. Eng. Chem.*, **3**, 629 (1911).

(11) Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163 (1900).

(12) Yost, THIS JOURNAL, **48**, 152 (1926).

(13) Lehrman, *J. Chem. Ed.*, **10**, 50 (1933).

[A CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF IDAHO]

Preparation and Properties of Silver Sols by Reduction of Silver Halides with Formaldehyde

BY T. IVAN TAYLOR AND WM. H. CONE

An analysis of some Bredig silver sols showed them to be unsuitable for some investigations recently begun. The precipitated colloid was found to contain from 26 to 44% of silver oxide depending, among other things, on the amount and kind of electrolyte used for stabilizing. Approximately a liter of the gases given off during the preparation of Bredig silver sols was collected and analyzed. The gases consisted of 22.1% oxygen and 77.9% hydrogen by volume. There was, therefore, an equivalent of 11.2% oxygen united with the silver to form silver oxide.

A silver colloid comparable in constitution and properties to Zsigmondy gold sols seemed desirable, so a method of reduction with formaldehyde without the use of a protective colloid was developed.

Experimental

It is well known that silver halides formed in excess of silver nitrate or alkali halide form stable positive and negative colloids, respectively. The angle of attack chosen was the reduction of these colloidal silver halides. The halide sols prepared with excess silver nitrate were reduced immediately forming a stable negative sol while those with excess halide were reduced only slowly and formed no stable sol.

Though the amounts of the reagents theoretically necessary were calculated, the solution to the problem was best found by trial and error

TABLE I

EFFECT OF VARYING AMOUNTS OF REAGENTS ON STABILITY AND PROPERTIES OF THE SILVER SOLS

Cc. of 0.1 *N* $AgNO_3$ (diluted to 250 cc.)	Cc. of 0.1 *N* KBr (diluted to 250 cc.)	Cc. of 2% Formaldehyde	Cc. of 0.3 *N* NaOH	Stability and properties of sol
10	9	20	0	No reduction
			3	Reddish-purple, cloudy, unstable
			10	Ruby-red, stable
			30	Dark, unstable
10	9	5	10	Dark, unstable
		10		Ruby-red, stable
		30		Ruby-red, stable (no effect)
10	0	10	10	Bluish-gray, unstable
	0.1			Bluish-gray, unstable
	.2			Straw-yellow, stable
	.3			Straw-yellow, stable
	1.0			Reddish-yellow, stable
	5.0			Reddish-yellow, stable
	9.0			Ruby-red, stable

methods. Table I gives a brief summary of the results as the amounts of the different substances were varied.

The procedure finally adopted for the preparation of a highly dispersed silver sol by this method is briefly summarized as follows. Dilute 10 cc. of 0.1 *N* silver nitrate to 250 cc. and add slowly with vigorous stirring 1 cc. of 0.1 *N* potassium bromide diluted to 250 cc. Add to the resulting mixture 10 cc. of 2% solution of formaldehyde; then add quickly with vigorous stirring 100 cc. of 0.03 *N* sodium hydroxide. Reduction takes place immediately after addition of the sodium hydroxide and the sol changes from a brownish-yellow by reflected light to a straw-yellow in about an hour. It then has a clear reddish-yellow color by transmitted light.

Hydroquinone was used with equal success but it has the disadvantage of giving a brown-colored oxidation product. A stable sol could not be prepared by replacing potassium bromide with potassium chloride, but potassium iodide worked equally well. A comparison of the properties of these sols, all prepared by the same method, is best given in Table II.

TABLE II

ANALYSIS AND PROPERTIES OF SOLS PREPARED FROM HALIDES

Halide salt,	cc.	Color of sol	Stability	Silver, %	Precipitation value mml. $NaNO_3$ per liter	Cataphoretic velocity $\times 10^5$ cm./sec./volt/cm.
KCl	1	Bluish-gray	Unstable	99.44	..	..
	9	Bluish-gray	Unstable	99.46	..	..
KBr	1	Reddish-yellow	Stable	99.03	40.0	42.2
	9	Ruby-red	Stable	98.26	12.0	41.7
KI	1	Brownish-red	Stable	82.75	44.0	41.7
	9	Bright ruby-red	Stable	4.32	88.0	39.9

The percentage of silver was determined by dissolving the silver in the precipitated sol with warm nitric acid. The residues in the cases of potassium bromide and potassium chloride were completely soluble in ammonia. Silver iodide is insoluble in ammonia. Warm ammonia poured over another precipitated sol made with 1 cc. of potassium bromide dissolved only 0.46%, indicating that silver bromide was dissolving from the surface, but may have been some silver oxide or silver hydroxide. At most, then, there is only very little, if any, silver oxide in the sol.

The precipitation values were made by diluting varying volumes of 0.1 *N* sodium nitrate to 15 cc. and mixing quickly with 10 cc. of the sol. The color change at the precipitation point is almost as marked as it is with Zsigmondy gold sols. The amount of electrolyte which causes complete precipitation within twelve hours causes the sols to change to a definite green within three to five minutes. The color changes by transmitted light after addition of precipitating electrolyte are as follows: orange-yellow ⟶ reddish-yellow ⟶ ruby-red ⟶ greenish-yellow ⟶ green ⟶ bluish-green ⟶ blue ⟶ bluish-lavender ⟶ purple ⟶ purple-gray ⟶ gray.

A sol prepared according to the above directions was dialyzed in cellophane bags for 108 hours in running distilled water (average conductance, 4.2×10^{-6}). The effect of the dialysis is given in Table III.

TABLE III

EFFECT OF DIALYSIS ON SILVER SOL

Sol	Cataphoretic velocity cm./sec./volt/cm.	Conductance, mhos	Precipitation value, millimoles of $NaNO_3$ per liter
Undialyzed	42.2×10^{-5}	5.14×10^{-4}	40.0
Dialyzed	40.7×10^{-5}	5.0×10^{-6}	24.0

Further tests on the properties and structure of these silver sols were made by diluting 10 cc. of 0.1 *N* silver nitrate to 500 cc. and reducing with formaldehyde and sodium hydroxide as before. Just as the color reached a milky purple, 2 cc. of 0.1 *N* solutions of various salts were added and their effect on the stability of the silver particles noted at various times. Some settled out comparatively rapidly while others settled only slowly, and some not at all. The apparent order of their stabilizing effect as judged from rate of settling and appearance after twenty-four hours is: unstable, NaOH, K_2CO_3, K_2SO_4, KCl, $K_2C_2O_4$, $KMnO_4$, $NaNO_2$; slightly precipitated, K_2CrO_4, Na_2SiO_3, $Na_2HPO_4(PO_4^{\equiv})$, $K_2Cr_2O_7(CrO_4^{=})$, KCN, KCNS; completely stable, KBr, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $Na_2S_2O_3(S^{=})$, Na_2S, K ethyl xanthate, KI.

The order is essentially that of the solubility of the silver salt normally formed with the anion. Most all anions which normally form a silver salt with a solubility of 0.002 g. per 100 g. of water or less stabilize the silver particles. Apparently at low concentrations of the anion, the more insoluble the silver salt, the greater is its stabilizing effect. The one most definitely out of place is the chloride ion. The true ionic radius of the chloride ion according to Goldschmidt is 1.33 Å. compared with 2.02 Å. for the iodide ion. In general, the smaller the ionic radius, the greater the hydration of the ion. Thus the moles of water per mole of chloride ion is two while for the iodide ion it is only one-half. The greater the hydration of the ion, the less will be the electrochemical attraction of the silver atoms in the crystal surface for that ion. The greater insolubility of the chloride ion is apparently overbalanced by its hydration, thus preventing adsorption of enough ions to give the required potential for stability.

Six liters of sols stabilized as above by chloride, bromide and iodide were prepared and precipitated. The washed and dried coagulum of each was analyzed as before. The warm nitric acid dissolved and carried through the crucible all the silver but enough to react with the halide carried down. The results are given in Table IV.

TABLE IV

ADSORPTION OF HALIDES BY SILVER

Halide sol	Pptd. colloid, g.	Undissolved residue of AgX, g.	Halogen, g.	Total weight of silver, g.	G. atoms of halogen per gram atom silver	Ratio of halogens adsorbed
AgCl	0.8733	0.0026	0.00064	0.8727	0.002243	1
AgBr	.9025	.0076	.0030	.8995	.004478	1.997
AgI	1.0383	.3738	.1604	.8779	.1293	57.66

If a regular stoichiometric chemical reaction of the simple double decomposition or replacement type had taken place on the surface, one would expect equivalent amounts to be carried down after allowing for the differences in solubility. This is definitely not the case. The process seems to be one governed more by the principles of electrochemical adsorption. The differences are readily explainable on the basis of hydration of the ions and insolubility as a measure of the electrochemical attraction between the atoms of the crystal surface and the ion adsorbed. Similar observations were made by Beckley and Taylor[1] on the adsorption of various substances on silver iodide. Besides adsorption in this type of system, however, one must not fail to recognize other types where the system is fundamentally different.[2]

There is a difference in the appearance, stability, and apparent degree of dispersion obtained when the stabilizing substance is added before reduction rather than after. For example, a sol prepared with 1 cc. of potassium bromide added before reduction is a clear reddish-yellow, while it is a milky, brownish-yellow when added after reduction. On adding the potassium bromide to the silver nitrate as directed above, no precipitate or coloration can be seen, but very minute particles of silver bromide must be present which act as reduction and condensation centers. The bromide ions liberated on the reduction of these silver bromide nuclei can then act as stabilizing ions on the surface of the reduced silver.

Summary

1. A method of preparing comparatively pure silver colloids by a reduction process has been described.

2. The properties and probable structure of these sols with analyses of sols prepared with different halides at varying concentrations have been given.

MOSCOW, IDAHO

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(1) Beckley and Taylor, *J. Phys. Chem.*, **29**, 942 (1925).

(2) *Cf.* Mukherjee, *Phil. Mag.*, [6] **44**, 338 (1922).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Ammonium Trinitride[1]

BY W. S. FROST, J. C. COTHRAN AND A. W. BROWNE

In connection with a current investigation of the nitridizing action of ammonium trinitride in solution and in the vapor state, determinations have been made of various properties of this substance, including (1) its solubility in water, methanol, ethanol, benzene and ether, (2) its qualitative behavior toward numerous organic liquids, (3) its specific gravity and the specific gravity of its saturated solutions and (4) its vapor tension at temperatures from 15 to 134°.

Preparation of Ammonium Trinitride.—The ammonium trinitride used throughout the present investigation was prepared either by the method of Browne and Houlehan,[2] or by the following procedure: 65 g. of sodium trinitride was placed in a 500-cc. round-bottomed flask connected through a Reitmeier bulb with a suitable condenser and a receiver containing 200 cc. of ether and cooled with ice. Two hundred cc. of water and 200 cc. of ether were added, and 60 cc. of concentrated sulfuric acid was slowly introduced, from a dropping funnel, beneath the surface of the solution. The greater part of the hydrogen trinitride, diluted with ether vapor, passed over into the receiver during this operation. The remainder was distilled by heating the flask for a short time over the steam-bath. The ethereal distillate was refluxed for thirty minutes over calcium chloride, and was finally redistilled from the desiccant. Dry ammonia gas was bubbled through the ethereal hydrogen trinitride until complete precipitation of the ammonium salt had been effected. The final product was readily freed from residual ether by storage over sulfuric acid.

Solubility of Ammonium Trinitride.—Curtius[3] observed that ammonium trinitride is soluble in water and in 80% ethanol, slightly soluble in 100% ethanol, and insoluble in ether and in benzene. Qualitative experiments have been performed by the authors with a number of other liquids at room temperature, including methanol, pyridine and glycerol, in which the salt is soluble; allyl, butyl and isobutyl alcohols, in which it is slightly soluble; and acetone, aniline, benzaldehyde, carbon disulfide, chlorobenzene, chloroform, ethyl acetate, ethyl methyl ketone, isoamyl alcohol, methyl acetate, nitrobenzene, tetrachloroethane, toluene and xylene, in which it is insoluble.

Quantitative determinations of the solubility of ammonium trinitride in carefully purified benzene, ether, ethanol, methanol and water have been made by a method and with an apparatus especially designed for systems in which both solvent and solute are

TABLE I

SOLUBILITY OF AMMONIUM TRINITRIDE

	Grams NH_4N_3 per 100 cc. soln.			*d* of satd. soln.		
Solvent	0°	20°	40°	0°	20°	40°
Benzene	...	0.0032	0.0078	....	0.8778	0.8609
Ether	...	.0063	.....	....	.7129	....
Ethanol	...	1.060	1.325	....	.7972	.7803
Methanol	...	3.268	3.984	....	.8166	.7986
Water	13.80	20.16	27.07	1.0435	1.0473	1.0554

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[1] This article is based upon parts of the theses presented by Walter Sprague Frost and John Cleveland Cothran to the Faculty of the Graduate School of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Browne and Houlehan, THIS JOURNAL, **33**, 1742 (1911).

[3] Curtius, *Ber.*, **24**, 3341 (1891).

volatile.[4] The results are summarized in Table I. Each datum is the average of at least two satisfactorily concordant determinations.

Specific Gravity of Solid Ammonium Trinitride.—Determinations of the specific gravity made with the aid of a pycnometer containing a saturated solution of the salt in benzene yielded the result d_{20} (compared with water at 4°) = 1.3459.

Vapor Tension of Ammonium Trinitride.—Curtius[3,5] and his co-workers have repeatedly called attention to the volatility of ammonium trinitride. From vapor density determinations Curtius and Rissom[5c] concluded that the vapor was completely dissociated at 100°.

The results of a series of measurements of the vapor tension of freshly sublimed ammonium trinitride at temperatures ranging from 15 to 134° are recorded in Table II. For this work a constant volume tensimeter with compact, completely immersible cell was designed.[6]

TABLE II

VAPOR TENSION OF AMMONIUM TRINITRIDE

Temp., °C.	Pressure		Diff., mm.	Temp., °C.	Pressure		Diff., mm.
	Obs., mm.	Calcd., mm.			Obs., mm.	Calcd., mm.	
15.0	0.2	0.3	−0.1	77.9	38.5	35.8	2.7
27.5	.6	.8	− .2	85.0	55.1	56.0	− 0.9
32.5	1.0	1.3	− .3	91.0	80.1	80.5	− .4
37.5	1.9	1.9	.0	96.0	108.3	107.9	.4
42.0	2.9	2.8	.1	102.9	160.9	160.0	.9
48.0	4.5	4.4	.1	109.0	222.7	223.9	− 1.2
54.0	6.7	6.9	− .2	114.0	292.3	291.8	0.5
58.4	9.5	9.5	.0	119.0	377.9	379.3	− 1.4
61.9	12.0	12.2	− .2	125.0	508.1	512.9	− 4.8
67.5	18.5	18.0	.5	132.1	709.9	727.8	−17.9
71.9	24.4	24.2	.2	134.2	782.1	803.5	−21.4

The equation used in calculating the pressures was: $\text{Log } p = -(3428.6/T) + 11.325$.

The rectilinear character of the logarithmic curve indicates the nonexistence of isomeric forms[7] of ammonium trinitride under the conditions prevailing in the experiments. This negative conclusion was strongly substantiated by the identity of the vapor tension curves successively obtained with samples of ammonium trinitride that had been (1) freshly prepared, but not sublimed, (2) stored for five months over calcium chloride, (3) stored for eight months in dry air containing ammonia gas and (4) freshly sublimed.

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(4) A detailed description of the method and apparatus used in this work will be found in the thesis, "A Study of Ammonium Trinitride," by W. S. Frost, of which a typewritten copy has been deposited in the Library of Cornell University, Ithaca, N. Y.

(5) Curtius, (a) *Ber.*, **23**, 3033 (1890); (b) Curtius and Radenhausen, *J. prakt. Chem.*, **43**, 208 (1891); (c) Curtius and Rissom, *ibid.*, **58**, 273 (1898).

(6) Thesis, "A Study of Certain Compounds Containing Chains of Four Nitrogen Atoms," by J. C. Cothran. A typewritten copy is on file in the Library of Cornell University, Ithaca, N. Y.

(7) Mendeléeff, *Ber.*, **23**, 3464 (1890).

When samples that had been stored for a long time over phosphorus pentoxide were sublimed, however, appreciable amounts of a white, vesicular, relatively non-volatile residue were obtained. This may be identical with the residual traces noted by Curtius and Rissom.[5c] It was at first surmised that this residue might be the long-sought isomer predicted by Mendeléeff.[7] Analysis by the Pregl method, however, proved that the substance was not a hydronitrogen, but rather, in all probability, an ammonium salt of hypophosphorous acid. It is interesting to note, further, that storage of ammonium trinitride over phosphorus pentoxide, calcium chloride or any other desiccant capable of absorbing ammonia but not hydrogen trinitride, soon results in the accumulation of considerable amounts of the latter substance in the vapor phase. The reverse is true for alkaline desiccants that selectively absorb hydrogen trinitride.

Summary

The solubility of ammonium trinitride (1) in water, methanol, ethanol, benzene and ether has been determined quantitatively and (2) in numerous organic liquids has been studied qualitatively. The specific gravity of solid ammonium trinitride and of various saturated solutions has been determined. The vapor tension of the solid has been measured over a temperature range of 15 to 134°.

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Solid–Liquid–Air Contact Angles and their Dependence upon the Surface Condition of the Solid

BY F. E. BARTELL AND ALLAN D. WOOLEY

Introduction

Several investigators[1] have observed that the angle formed when a contact angle forming liquid has advanced to rest over a dry solid surface is larger than the angle formed when the liquid has receded to rest from a wetted surface. Sulman[1d] called this phenomenon "hysteresis of contact angle," which term was used to imply that advancing and receding contact angles are unstable forms of a definite equilibrium contact angle. Later workers,[1e,2] holding similar views, have attempted to evaluate equilibrium contact angles by relating them mathematically to the advancing and receding contact angles. Thus Ablett, believing that the so-called

(1) (a) Edser, Fourth Report of Colloid Chem., 284 (1922); (b) Rayleigh, *Phil. Mag.*, **30**, 397 (1890); (c) Pockels, *Physik. Z.*, **15**, 39 (1914); (d) Sulman, *Trans. Inst. Min. & Met.*, Nov. (1920); (e) Adam and Jessop, *J. Chem. Soc.*, **127**, 1865 (1925).

(2) Ablett, *Phil. Mag.*, **46**, 244 (1923); Nietz, *J. Phys. Chem.*, **32**, 255 (1928).

hysteresis of contact angle is due to adsorption of the liquid by the solid, concluded that the "stationary angle" is the arithmetical mean of the dynamic advancing and receding contact angles. Adam and Jessop consider that the difference between advancing and receding contact angles lies in a "simple friction" effect between the liquid and the solid, and assume that the cosine of the equilibrium angle is equal to the mean of the cosines of the advancing and receding angles. Others have expressed the view that with proper precautions "equilibrium" contact angles can be obtained directly and measured as such.[3] Proof of the existence of a single and definite equilibrium contact angle, however, has not been given, nor has any definite relationship between the theoretical equilibrium contact angle and the observed static advancing and receding angles been established.

The purpose of the present investigation was to study the characteristics of static advancing and receding contact angles and to determine if possible their relation to the "equilibrium" contact angle. The results obtained indicate that both the advancing contact angle and the receding contact angle may exist as stable and characteristic angles for the precise system in question.

Experimental

The general capillary formulation used for calculation of surface tension values in cases in which the liquids form a contact angle with the walls of the capillary is $S = rhdg/2 \cos \Theta$, in which S represents the surface tension of the liquid, r the radius of the capillary, h the height of liquid ascension, d the density of the liquid, g the gravitational constant, and Θ the contact angle. Thus, by measurement of the capillary rise of a liquid forming a contact angle in a capillary of known radius, the contact angle can be calculated if the true surface tension of the liquid can be obtained by some method which gives true values independent of the contact angle. The only method independent of contact angle which seemed sufficiently accurate for this purpose was the drop weight method as developed and standardized by Harkins and co-workers. Accordingly, that method was adopted for this investigation. The liquids selected were α-bromonaphthalene and acetylene tetrabromide. The solids selected were "Pyrex" and silica.

Apparatus

The Capillary Height Method.—The details of apparatus and operation necessary to obtain results of high accuracy with the capillary height method are fully discussed by Richards and Coombs,[4] Richards and

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(3) Langmuir, *Trans. Faraday Soc.*, **15**, 62 (1920); Bartell and Merrill, *J. Phys. Chem.*, **36**, 1178 (1932).

(4) Richards and Coombs, THIS JOURNAL, **37**, 1656 (1915).

Carver[5] and Harkins and Brown.[6] The apparatus used by us is illustrated in Fig. 1.

The apparatus used for the determination of the drop weight was modeled, in its essential details, after that described by Harkins and Brown.[6] It was used in an air thermostat which made some minor alterations advisable (see Fig. 2).

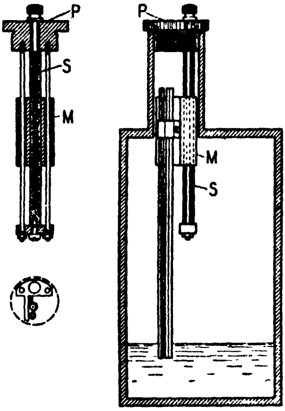

Fig. 1.—Capillary height apparatus.

The air thermostat was used with both methods. During the time of a series of observations the temperature of the liquid under measurement never varied more than 0.03°.

Density Determinations.—The density data appearing in the literature for α-bromonaphthalene and acetylene tetrabromide show such discrepancies[7] that densities of these liquids were determined. Values were determined over small temperature ranges so that the density at the working temperature could be obtained by linear interpolation. A new pycnometer was devised which greatly reduced the labor necessary in determining a series of densities over a given temperature range.

The details of the pycnometer are shown in Fig. 3. The new feature of the pycnometer is that it can be tightly closed so as to eliminate evaporation losses. This is effected by the use of copper-to-glass seals upon the inlet and outlet tubes which makes it possible to use screw-caps fitted with lead gaskets. The pycnometer is used as a constant-weight volume-determining apparatus.

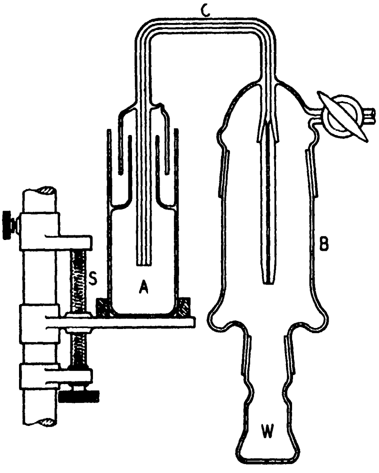

Fig. 2.—Drop-weight apparatus.

Procedure and Measurements.—It was our belief that in former investigations the pretreatment of the solid surface upon which contact angle measurements were made had not been sufficiently investigated, and that the cause of apparent anomalies and of the so-called "hysteresis contact angle" might lie therein.

The preliminary work indicated that although the magnitude of the advancing contact angle was dependent upon the precise pretreatment of the solid surface upon which it was measured, the magnitude of the receding contact angle was largely independent of the pretreatment of the solid surface. This suggested that it might be possible by proper pretreatment to obtain a solid surface

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(5) Richards and Carver, This Journal, **43**, 827 (1921).

(6) Harkins and Brown, *ibid.*, **41**, 499 (1919).

(7) Patterson and Thompson, *J. Chem. Soc.*, **93**, 366 (1908); Walden and Swinne, *Z. physik. Chem.*, **82**, 271 (1913); Harkins, Clark and Roberts, This Journal, **42**, 700 (1920); Harkins and Feldman, *ibid.*, **44**, 2665 (1922).

TABLE I

DENSITY AND SURFACE TENSION DATA FOR α-BROMONAPHTHALENE AND ACETYLENE TETRABROMIDE

α-Bromonaphthalene			Acetylene tetrabromide		
Temp., °C.	Density, d_4^t	Surface tension, dynes/cm.	Temp., °C.	Density, d_4^t	Surface tension, dynes/cm.
17.4	1.4854	44.88	20.0	2.9638	49.44
20.1	1.4826	44.53	23.0	2.9571	
25.23	1.4774	43.89	25.4	2.9518	48.65
25.24	1.4773		27.3	2.9479	
26.3	1.4763				
30.02	1.4726	43.28			

upon which the advancing contact angle would be equal to the receding contact angle. Such surfaces were finally produced.

The capillaries used were first given a rigorous acid cleaning with concentrated nitric acid, were then washed with a large quantity of distilled water (steamed with water for at least three hours), dried and calibrated, again treated with nitric acid and washed. After this second acid cleaning, acid was never used again in recleaning the capillaries. After use the capillaries were cleaned each time by drawing liquids through them. The order of treatment was first, ether or benzene, then benzene and then acetone. Usually about 100 cc. of each liquid was used, after which a quantity of distilled water was drawn through.

After being cleaned as described above, the capillaries were given one of the following pretreatments: (1) steamed with water for one hour. Heated in a current of clean, dry air at a certain temperature (shown in the data) for a given time. (2) Flushed with benzene vapor for one hour. Heat treated at a known temperature for a given time in a current of clean, dry air.

After the capillaries had been heat treated at an elevated temperature (425°),[8] the furnace was slowly cooled over a period of one hour (to 300°), after which it was disconnected and allowed to cool fairly rapidly. As soon as the capillary had reached the temperature of the thermostat (one-half to one hour) it was lowered into the liquid very slowly to avoid wetting above the meniscus. The height of the large meniscus was taken and subsequently the height of the lowest point of the small meniscus. The capillary was then lowered further into the liquid and the meniscus caused to advance up the dry capillary. Again, after equilibrium had been reached, the capillary height was measured. Usually six such advancing heights, and then a series of six receding heights, were measured. Each series of six measurements was averaged to give a single advancing or receding capillary height. At least three series of measurements were run for both advancing and receding heights for each method of pretreatment. Corrections were made for meniscus effects when determining capillary height values.

Before confidence could be placed in the values of the contact angles calculated by comparison of the apparent surface tension

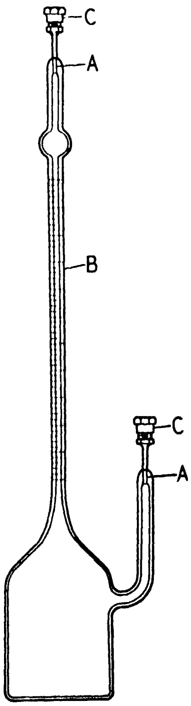

Fig. 3.—Pycnometer: A, copper-to-glass seals; B, tube graduated to 0.01 cc.; C, metal cap with lead jacket.

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[8] Careful investigation showed that the radii of both Pyrex and silica capillaries remained unchanged even after heating the capillary for one hour at 450°.

as measured by the capillary height method with the true surface tension as measured by the drop-weight method, it was necessary to prove that the two apparatuses gave the same surface tension value when a zero contact angle liquid was used. For this purpose benzene was selected.

The surface tension at 25.23° of very carefully purified benzene was determined by the capillary height method using both Pyrex and silica capillaries. The capillaries were carefully cleaned, flushed with benzene vapor for one hour and finally heated for one hour at 425°. Advancing and receding capillary heights were measured. The values obtained in the Pyrex capillary were as follows: the average of all the advancing heights gave 28.165 dynes/cm.; the average of receding heights gave 28.16 dynes/cm.; the average of advancing heights in the silica capillary gave the value 28.18 dynes/cm., and the average of receding heights gave 28.16. The mean of these values gives the surface tension of benzene at 25.23° as 28.166. The drop-weight method using a dropping tip having a radius of 0.29835 cm. gave 28.175 dynes/cm. as an average value of the surface tension of the same sample of benzene at 25.23°.

Discussion of Results

Influence of Pretreatment.—Tables II and III give, respectively, the advancing and receding contact angle values obtained for the systems α-bromonaphthalene–Pyrex (and silica)–air, and acetylene tetrabromide–Pyrex (and silica)–air by measurements in capillaries treated in the manner indicated in the tables as "Pretreatment." Inspection of the tables shows that for a particular vapor treatment such as steaming with water, the magnitude of the advancing contact angle depends upon the temperature and duration of heat treatment. Taking the results in Table II as typical, it is seen that the advancing contact angle of α-bromonaphthalene in a Pyrex capillary which had been steamed with water and heat treated at 115° for fifteen minutes is 24°. If during pretreatment the capillary is heated at 125° for one hour, an angle of 18° is obtained. Heating for twenty-four hours at 125° gives an angle of 16°. With longer heating of the capillary at 125° during pretreatment, the contact angle remains sensibly constant. If the capillary is pretreated by heating for one hour at 425°, the advancing angle becomes zero. The calculated cosine of the angle (0.99946) is equivalent to an angle of 1°53′, but since the error of measurement for an angle of zero degrees magnitude is equivalent to a 3° angle, the angle 1°53′ is sensibly zero. The advancing contact angle of α-bromonaphthalene on a Pyrex surface pretreated by steaming with water and subsequently by heat treating at 425° for one hour has been proved by us (using the Richards and Carver test) to be a zero contact angle. Pretreatment of the capillary at elevated temperatures tends to cause a decrease of the advancing contact angle. Heat treatment of a capillary at a given temperature lowers the advancing contact angle rapidly during the first hour, after which longer times of heating leave it sensibly constant.

The same generalizations apply if the capillary is vapor-flushed with benzene rather than with water. It should be noted, however, that a Pyrex capillary steamed with water and heated at 125° for one hour gives

TABLE II

ADVANCING AND RECEDING CONTACT ANGLES FOR THE SYSTEMS α-BROMONAPHTHALENE-PYREX-AIR AND α-BROMONAPHTHALENE-SILICA-AIR

t, 25.23° $S = 43.89$ dynes/cm. $(D^t_4 - d) = 1.4762$

Advancing Capillary Heights

Pretreatment			Pyrex		Silica	
Vapor treatment of capillary steamed for 1 hr.	Heat treatment temp., °C.	Time of heating	Av. corr. height, cm.	θ_a	Av. corr. height, cm.	θ_a
Water	115	15 min.	2.740	24°	1.809	24°
Water	125	1 hr.	2.86	18°	1.828	22° 30′
Water	125	24 hr.	2.903	16°		
Water	425	1 hr.	3.010	0°[b]	1.967	6°[a]
Benzene	125	1 hr.	2.910	15°	1.907	15° 30′
Benzene	125	24 hr.			1.915	14° 30′
Benzene	425	1 hr.	3.010	0°[b]	1.969	5° 30′[a]

Receding Capillary Heights

				θ_r		θ_r
Water	115	15 min.	2.977	8° 23′	1.956	8° 30′
Water	125	1 hr.	3.008	0°[b]	1.969	5°[a]
Water	125	24 hr.	3.009	0°[b]		
Water	425	1 hr.	3.011	0°[b]	1.969	5° 30
Benzene	125	1 hr.	3.010	0°[b]	1.960	7° 30
Benzene	125	24 hr.			1.971	5°
Benzene	425	1 hr.	3.011	0°[b]	1.969	5°

[a] Proved to be finite by Richards and Carver method.

[b] Proved to be zero by tests made with the Richards and Carver method.

an advancing contact angle of 18° with α-bromonaphthalene, while an angle of 15° is obtained if the capillary is flushed with benzene and heated under the same conditions. The data show similar results for the systems α-bromonaphthalene-silica-air, acetylene tetrabromide-Pyrex-air and acetylene tetrabromide-silica-air.

The receding contact angles for the same systems and for the same pretreatments are also given in the tables. Taking the data for the receding contact angles of α-bromonaphthalene-silica-air as typical (Table II), one observes that the receding contact angle is largely independent of the pretreatment. Even insufficient drying (25°) was shown to have comparatively small effect upon the magnitude of the receding contact angle.

The data show that for the system α-bromonaphthalene-Pyrex (and silica)-air the same or very nearly the same advancing and receding contact angles are obtained, if the capillaries are pretreated by steaming with water or flushing with benzene and heat treated at 425° for one hour. This contact angle must be characteristic of the system, for it fulfils the most rigid requirement for an equilibrium contact angle—namely, that the same angle be obtained when the liquid advances to, and recedes to, equilibrium. The advancing contact angle of a system can, then, become equal to the receding contact angle, which is independent (apparently) of pretreatment; the receding contact angle must, therefore, be the most characteristic contact angle of a system.

Table III shows that for the systems acetylene tetrabromide–Pyrex (or silica)–air, the advancing and receding contact angles are not quite equal when the capillaries are heated during pretreatment for one hour at 425°. Subsequent experiments, in which silica tubes were heated to 600° for one hour in their pretreatment, gave for advancing and receding contact angles for the system silica–acetylene tetrabromide–air values which were sensibly the same.

TABLE III

ADVANCING AND RECEDING CONTACT ANGLES FOR THE SYSTEMS ACETYLENE TETRABROMIDE–PYREX–AIR AND ACETYLENE TETRABROMIDE–SILICA–AIR

t, 25.04° $S = 48.72$ dynes/cm. $(D^{t}_{4} - d) = 2.9513$

Advancing Capillary Heights

Pretreatment			Pyrex		Silica	
Vapor treatment of capillary steamed for for 1 hr.	Heat treatment temp., °C.	Time of heating	Av. corr. height, cm.	θ_a	Av. corr. height, cm.	θ_a
Water	25	15 min.	1.495	27°	1.063	15°
Water	140	3 hr.	1.546	21°	1.072	12°
Water	425	1 hr.	1.609	15°	1.0853	10°
Benzene	140	24 hr.	1.617	14°	1.046	18°
Benzene	425	1 hr.	1.622	13°	1.0651	14°
		Receding Capillary Heights				
				θ_r		θ_r
Water	25	15 min.	1.660	7°	1.079	11°
Water	140	3 hr.	1.647	10°	1.086	9°
Water	425	1 hr.	1.6496	9° 15′	1.0866	9° 30′
Benzene	140	24 hr.	1.649	9° 30′	1.086	9°
Benzene	425	1 hr.	1.6486	9° 30′	1.0862	8° 30′

The dependence of the advancing contact angle upon the treatment history of the solid surface suggests that in an advancing contact angle we have a very sensitive criterion of the surface condition of a solid.

During the course of the investigation the question arose—will a capillary which has been well wetted with a liquid and then drained by gravity, give an advancing height with that liquid equivalent to the receding height in the wetted capillary? This was tested for the systems α-bromonaphthalene–Pyrex–air and α-bromonaphthalene–silica–air as follows. The capillaries were cleaned in the usual manner, steamed for one hour with water, heated at 125° for one hour, cooled and then wetted with α-bromonaphthalene. The capillaries were then allowed to drain for twelve hours in an atmosphere saturated with α-bromonaphthalene. The advancing height of the liquid was then measured in the capillaries. It was found that advancing heights in capillaries treated in this manner were easily reproducible. The advancing contact angle for α-bromonaphthalene in a

Pyrex capillary treated as described was found to be 13°, and for α-bromonaphthalene in a silica capillary treated in an identical manner, 21°. Comparison with the corresponding receding contact angles, 0 and 5°, respectively, shows the advancing contact angles to be considerably larger in magnitude.

Theoretical Considerations.—The magnitude of the contact angle which a given liquid will form with a solid surface depends upon the relative values of the existing interfacial tension forces of the system. For any given set of interfacial energies there is a corresponding equilibrium configuration for the system; the contact angle formed may be either zero or finite. If any one of the free surface energies be changed, the contact angle (if finite) will change to a new characteristic value. This will be readily understood by considering Young's[9] equation[10] $S_1 - S_{12} = S_2 \cos \Theta$, for a drop at rest and in equilibrium upon a solid surface. It is seen that the magnitude of the contact angle is dependent upon the relation of the interfacial tensions at the solid-air (S_1), liquid-air (S_2) and solid-liquid (S_{12}) interfaces. If contamination of the system is prevented, the interfacial tensions of the solid-liquid and liquid-air interfaces remain constant. A difference in magnitude between an advancing contact angle and receding contact angle for two different samples of the same uncontaminated system is indicative that the free surface energy of the solid (against air) is different in the two cases.

In explanation of the results obtained in this investigation the problem to be dealt with seems to be the cause of the free surface energy changes in the solid-air interface. The particular pretreatment methods used in preparation of the solid surfaces were of such nature that two closely related processes undoubtedly contributed to the final state of the solid surface, namely, sorption and change in surface structure. By the term "sorption" is meant the collective result of the processes of adsorption and persorption. There is evidence that the processes of adsorption and persorption are accompanied by a change in structure of the sorbent solid.[11] Moreover, there can be little doubt that solids subjected to heat treatment at elevated temperatures undergo a change in surface structure.[12] The precise condition of a solid surface depends in fact upon every process to which it has been subjected during its preparation.

Penetration of gases or liquids to a finite distance into a solid surface (termed "persorption"[13]) must result in a change in the free surface energy

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(9) Young, *Phil. Mag.*, 165 (1805).

(10) The symbols S_1, S_{12} and S_2 represent, respectively, the surface and interfacial tension values of the solid-air, solid-liquid and liquid-air interfaces. Since free surface energy values are numerically equal to surface tension values, the relations of the equation are fulfilled equally well by free surface energy values.

(11) McBain, "The Sorption of Gases by Solids," Routledge, London, 1932; Bangham, *Phil. Mag.*, [7] **5**, 737 (1928).

(12) Beilby, "Aggregation and Flow of Solids," The Macmillan Company, New York, 1921.

(13) McBain and Britton, THIS JOURNAL, **52**, 2198 (1930).

of the solid–air interface by alteration of the forces of adhesion and by modification of the intermolecular cohesive forces existing between the molecules of the solid. The processes of sorption and of structural change are in most cases so intimately related that the individual effects cannot be isolated.

It has been shown,[14] by investigations on the adsorption of gases, that the surface of a solid in the amorphous form possesses a more intense field of surface force and a greater free surface energy than a crystalline form of the solid. Further, Beilby[12] has shown that the condition of a solid surface can be altered greatly by very simple treatments, such as heat treatment and subjection to solvents.

An advancing contact angle formed by a given liquid upon such an amorphous surface of a given solid would tend toward a minimum value for that solid–liquid system. A silica or Pyrex surface which has been subjected to sorption processes possesses a lower free surface energy, and as a result the advancing contact angle formed upon it by a given liquid would tend toward a maximum value.

The solid surface upon which a receding contact angle is formed is one which has had, in effect, an additional (and final) pretreatment process included in its preparation, namely, it has been wetted by the liquid under measurement. The independence of the receding contact angle from the initial pretreatment of the solid surface becomes more readily understood by consideration of this fact, for the final pretreatment process of a surface upon which a receding contact angle is formed is always the same. Wetting a solid surface by a liquid is apparently a very powerful pretreatment process, for it alters the effects of such other pretreatment processes as vapor flushing and low temperature heat treatment. Sorption and change in surface structure processes may occur when the solid surface is wetted by the liquid. The wetting liquid probably causes desorption of previously sorbed molecules. Likewise, the wetting liquid may cause a change in surface structure of the solid by exerting orientational and adhesional forces upon the surface molecules of the solid. The constancy of the receding contact angle of a given solid–liquid–air system suggests that a solid surface which has been wetted by a liquid is left in a definite condition with its characteristics determined by the wetting liquid used.

To account for the difference between advancing and receding angles in a single system one may conclude then that the advancing angle is dependent upon the precise condition (*i. e.*, the pretreatment) of the unwetted solid surface upon which the liquid is advancing, while the receding angle is largely independent of the pretreatment (*i. e.*, of the type described herein) of the solid surface. The liquid as it recedes leaves the solid surface in a definite and characteristic condition.

(14) Langmuir, *Phys. Rev.*, **8**, 149 (1916); Kuster, "Lehrbuch d. allg. Physik," 1916, p. 189, Pawlow, *Z. physik. Chem.*, **88**, 316 (1920).

When the advancing and receding angles in a system are found to be the same, it must be that the pretreatment of the surface has been so adjusted (through changes in sorption and orientation) as to give to the solid surface approximately the same characteristic condition as that imparted to it by wetting by the liquid in question.

The apparent anomalies and the so-called hysteresis of contact angles have caused certain investigators to propose concepts which describe the contact angle as an unstable configuration of a solid–liquid–air system. To the authors it seems that a careful consideration of the free surface energy relationships of such a system (particularly of the changes which may occur in the existing value of the solid–air interfacial free surface energy) explains the phenomena which seem to present anomalies and "hysteresis effects." To us it seems that a contact angle formed by a system whether advancing or receding is in effect an equilibrium contact angle and is characteristic of the system precisely as it then exists.[15] The contact angle formed by a system is then an extremely sensitive criterion of the energy relations existing in the system. Any variation in its magnitude points to the occurrence of some process which has caused a change in one or more of the interfacial energy values.

Summary

Certain conclusions which seem justifiable can be drawn from the data obtained in this investigation.

1. The magnitude of the advancing contact angle is intimately related to the treatment history of the solid surface upon which it is measured. A standard method of treatment of a solid surface results in a characteristic reproducible advancing contact angle with a given liquid. Because of the reproducibility and apparent stability of such contact angles they are in effect equilibrium angles. Advancing contact angles are very sensitive criteria of the condition of a solid surface.

2. The magnitude of receding contact angles is largely independent of the treatment history of the solid surface upon which they are formed. Receding contact angles are equilibrium angles and are the most characteristic of contact angles for a given solid–liquid pair.

3. A characteristic equilibrium contact angle exists for the system α-bromonaphthalene–silica–air and acetylene tetrabromide–Pyrex (or silica)–air which can be approached from either direction, *i. e.*, advancing liquid or receding liquid. This is the most characteristic contact angle for a given solid–liquid pair and is equivalent to the receding contact angle.

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(15) The advancing contact angle may not represent a true equilibrium angle in the strict sense of that term, but does represent a relatively stable angle which will not change appreciably with time. Its tendency to change is dependent upon the tendency of the solid phase (or surface) to pass to a more stable form (or condition) which can exist at a lower energy level.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Liquid Ammonia as a Solvent. III. The Solubility of Inorganic Salts at 25°

BY HERSCHEL HUNT AND L. BONCYK

In order to investigate the behavior of strong electrolytes in liquid ammonia it is advantageous to know their solubilities. It is the purpose of this article to report the solubilities of some inorganic salts in liquid ammonia at 25°.

Experimental

The same methods of measuring solubilities were used as described in the first paper of this series.[1] In the meantime, the vapor pressures of ammonia solutions of the salts of ammonia were determined and the following agreement between the two methods of measuring solubilities was found.

	NH_4NO_3	NH_4I
Solubility by vapor pressure	390.0 g.	368.5 g./100 g. NH_3
Solubility by methods of Paper I	390.0 g.	368.5 g./100 g. NH_3

M. Linard and M. Stephan[2] criticized our values as being too low because a vapor correction was not applied. The solubilities of the alkali halide salts were checked by weighing the amount of salt previously reported into a 25-mm. tube with the reported amount of ammonia, drawing the tube down to a long narrow capillary, sealing, and, when the salt had dissolved, weighing the tube. Then the tube was cooled, the tip broken and a few milligrams of ammonia allowed to escape. The tube was then placed in the 25° bath. Crystals always came out with this smaller amount of ammonia. The tubes were sealed as close to the liquid as possible. Using our method we found a value of 12.85 g./100 g. NH_3 for the solubility of sodium chloride at 0°. Linard's data show that we have a great variation in solubility with change in temperature. G. Patscheke[3] has shown that sodium chloride has a wide variation in solubility at various temperatures. Linard's results show that the vapor phase correction is no greater than was explained in Paper I.

We have taken special precautions to have all our materials extremely dry. Reagent grade chemicals were recrystallized three times from water and then from a suitable anhydrous solvent. They were dried to constant weight in a vacuum oven.

The formulas for ammonium oxalate, ammonium sulfate and sodium sulfate were incorrectly printed in the first paper of this series, subscripts of three being given instead of four. The solubility of sodium sulfate was incorrect also.

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(1) Hunt, THIS JOURNAL, **54**, 3509 (1932).

(2) M. Linard and M. Stephan, *Z. physik. Chem.*, **163**, 185 (1933).

(3) G. Patscheke, *Z. physik. Chem.*, **163**, 340 (1933).

TABLE I

THE SOLUBILITY OF INORGANIC SALTS IN LIQUID AMMONIA AT 25°

Substance	G./100 g. NH_3	Substance	G./100 g. NH_3	Substance	G./100 g. NH_3
$NH_4C_2H_3O_2$	253.16(?)	$KBrO_3$	0.002	$LiNO_3$	243.66
NH_4HCO_3	0.00	$KClO_3$	2.52	Li_2SO_4	0.00
NH_4ClO_4	137.93	KIO_3	0.000	MnI_2	.02
NH_4I	368.5	AgBr	5.92	$NaNH_2$	.004
$(NH_4)_2HPO_4$	0.00	AgCl	0.83	Na_2SO_4	.00
$(NH_4)_2S$	120.0	AgI	206.84	$Sr(NO_3)_2$	87.08
$BaCl_2$	0.00	$AgNO_3$	86.04	ZnI_2	0.10
$Ba(NO_3)_2$	97 22	$Ca(NO_3)_2$	80.22	ZnO	.00
KNH_2	3.6	H_3BO_3	1.92		

$SbBr_3$, $BiCl_3$, $Bi(NO_3)_3$, $Cd(NO_3)_2$, $Co(NO_3)_2$, $FeBr_3$, $Pb(C_2H_3O_2)_2$, Mg_3N_2, $Hg(NO_3)_2$, $Ni(NO_3)_2$, S, $SnCl_4$ appear to be insoluble, while $Cu(NO_3)_2$, I_2, $Pb(NO_3)_2$, and HgI_2 were very soluble in liquid ammonia but all reacted with ammonia.

If salts are ionized in ammonia as in water, salts with common ions should decrease each other's solubility and salts without common ions should increase the solubility of each other. This point was verified by determining the solubilities of the mixtures given in Table II: 0.2500 g. of the less soluble salt was mixed with variable amounts of the more soluble salt and ammonia added in excess. Ammonia was allowed to escape from the solution until a single small crystal of one salt came out of solution. Identical results were obtained by approaching the saturation point from opposite sides. The various experiments indicate the ratio of the two salts present in the solution when the solution was saturated with respect to one salt.

TABLE II

SOLUBILITIES OF MIXED SALTS

Moles Salt/10 moles NH_3

NaCl ⟷	$NaNO_3$	NH_4Cl ⟷	NH_4NO_3	NaCl ⟷	NH_4NO_3
0.0	1.95	0.0	8.2875	0.088	0.0
.0524	1.80	.4875	7.82	.534	1.562
.059	1.787	.576	7.70	.667	5.85
.0686	1.694	.692	7.4	.632	7.39
.0686	1.694	.734	6.54	.655	8.60
.0700	1.482	.903	4.83	.484	8.50
.0746	1.232	2.27	1.52	.0	8.2875
.087	0.46	3.01	0.255		
.088	.0	3.257	.0		

Discussion of Results

In general, the solubility of the halides increases as the atomic weight of the halogen increases. The salts of ammonia are the most soluble, salts of lithium are more soluble than salts of sodium, salts of sodium are more soluble than salts of potassium, and the solubilities of the nitrates of the alkaline earths decrease as the atomic weight of the metal increases. The halides of silver diverge the most radically of any salts from the aqueous solubilities, the iodide being 7.5 × 10^8 times as soluble in ammonia as in water. Silver iodide reacts with silver nitrate so that the solubility of mixtures of the two salts could not be determined. Mixtures of sodium nitrate and ammonium chloride react with explosive violence. All sulfates, phosphates, carbonates and oxides tested were insoluble. On comparing the solubilities of silver halides or any sulfates, one sees no correlation between physical properties and solvent power of the two solvents. As a general rule, the inorganic salts studied are more soluble in ammonia than in the aliphatic alcohols.

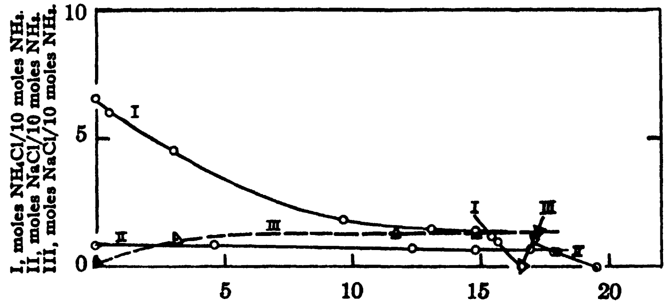

Fig. 1.—Solubilities of mixed salts: I, moles NH_4NO_3/10 moles NH_3 (scale 1 mole = 2 cm.); II, moles $NaNO_3$/10 moles NH_3 (scale 1 mole = 1 decimeter); III, moles NH_4NO_3/10 moles NH_3 (scale 1 mole = 2 cm.).

Some salts are very soluble but are unstable in liquid ammonia, as lead nitrate, while others, as nickelous nitrate, react only after a certain concentration is reached. The difference in solubility between similar salts, as potassium iodide and potassium iodate, makes this solvent a possible one to use for extractions in the preparation of pure chemicals. Compounds of the metals of groups I and II of the periodic table show the least tendency toward reaction with ammonia in liquid ammonia.

Figure 1 shows that the presence of a common ion decreases the solubility of a salt in ammonia. Curve III shows that salts without a common ion increase the solubility of each other. The solubility curves have the same general shape in ammonia as in water, indicating ionization of the salts.

Summary

1. The solubilities of twenty-six inorganic compounds in liquid ammonia have been determined quantitatively at 25°.

2. The solubilities for three sets of mixed salts, NH_4Cl–NH_4NO_3, NaCl–$NaNO_3$, and NaCl–NH_4N[illegible] have been determined.

LAFAYETTE, INDIANA

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Further Studies on Acetic Acid–Acetate Solutions

BY ARTHUR W. DAVIDSON AND WILBERT CHAPPELL

Introduction

The purpose of this investigation was to supplement the existing data on the solubility of acetates in anhydrous acetic acid[1] by the study of two additional acetates, namely, those of strontium and nickel, each of which presented certain points of interest.

It was to be expected,[1b] in the case of strontium acetate, that the solid phase in equilibrium with the solutions at ordinary temperatures would be a solvate, and that the solubility of this compound would be intermediate between that of barium and that of calcium acetate. In the case of nickel acetate, previous statements as to solubility have been extremely conflicting. Spaeth[2] stated that this salt was easily soluble in acetic acid, but Adler[3] reported its solubility as only 0.44 mole per cent. even at 140°, and Schall and Markgraf[4] gave a figure of 0.1971 normal (0.60 mole per cent.) for the concentration of a solution which they apparently considered saturated at 65°.

A study was made also of the effect of ammonium acetate upon the solubility of nickel acetate, in the expectation that this ternary system would be analogous to the ammonium acetate–cupric acetate–acetic acid solutions previously described.[1c]

Method

Preparation of Materials.—Acetic acid (m. p. 16.55–16.62°) and ammonium acetate were prepared as described in previous papers. Strontium acetate prepared from strontium carbonate was recrystallized from dilute acetic acid and the product kept at 165° for four days. Nickel acetate was prepared similarly. The recrystallized tetrahydrate was dehydrated at 90°, the product moistened with pure acetic acid and again heated at the same temperature to constant weight. The pale green anhydrous salt was analyzed for nickel by means of dimethyglyoxime, giving 33.11% as compared with the calculated 33.21%.

Strontium Acetate–Acetic Acid System.—Freezing points were determined by the synthetic method described in previous articles. The freezing points of the acetic acid are believed to be correct to ±0.2°, other equilibrium temperatures to ±0.5°.

Nickel Acetate–Acetic Acid System.—It soon became apparent why the recorded data for the solubility of nickel acetate had been so discordant. The salt dissolved fairly readily on gentle heating, the solutions showing a faint turbidity which did not disappear at higher temperatures. When the concentration of solute was less than 12 mole per cent., only acetic acid was obtained as solid phase on cooling. Solutions containing 12 to 13 mole per cent. of solute, however, deposited abundant quantities of a finely

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(1) (a) Kendall and Adler, THIS JOURNAL, **43**, 1470 (1921); (b) Davidson and McAllister, *ibid.*, **52**, 507, 519 (1930); (c) Davidson and Griswold, *ibid.*, **53**, 1341 (1931).

(2) Spaeth, *Monatsh.*, **33**, 235 (1912).

(3) Adler, Thesis, Columbia University, 1920.

(4) Schall and Markgraf, *Trans. Am. Electrochem. Soc.*, **45**, 161 (1924).

divided greenish-white solid, which did not redissolve even on heating to the boiling point. The extreme slowness with which equilibrium was attained in these solutions (if, indeed, it was a true equilibrium) eliminated all possibility of employing the synthetic method for determining solubility. There remained as an alternative the analysis of solutions apparently saturated at a fixed temperature. Accordingly, a 13 to 14% solution was prepared at 100°; on slow cooling, a solid phase appeared. The mixture was then kept at 30° in a thermostat, with frequent stirring, for twelve hours, after which some of the solution was drawn off through a Gooch crucible provided with a thick mat of asbestos. The filtering device remained immersed in the thermostat throughout the filtration, precautions being taken to exclude moisture. The concentration of the filtrate was determined by analysis for nickel by the dimethylglyoxime method.

Ammonium Acetate–Nickel Acetate–Acetic Acid System.—The same difficulty was encountered here as in the case of the binary solutions just referred to, namely, that the solid phase, although it separated readily enough from supersaturated solutions, redissolved only extremely slowly. The same procedure was therefore employed as in the binary system. Solutions containing both ammonium and nickel acetates were prepared at elevated temperatures and allowed to come to equilibrium at 30°. After filtration, the nickel content of the solution was determined as before, while another portion of the filtrate was analyzed for ammonium by making it alkaline with sodium hydroxide solution and distilling the ammonia into standard hydrochloric acid. The concentration of acetic acid could then be found by difference.

Analysis of Solid Phases.—The desired solid having been obtained by the cooling of a solution of suitable concentration, the mother liquor was filtered off by suction, and the crystals rapidly dried between porous tiles. In the case of strontium acetate, the product was analyzed for acetic acid by titration with sodium hydroxide solution. In the product containing nickel acetate, nickel was determined by means of dimethylglyoxime, and in the ternary system the solid was analyzed for both nickel and ammonium, as in the case of the corresponding solutions.

Results

I. System $Sr(C_2H_3O_2)_2$–$HC_2H_3O_2$.—Concentrations in mole per cent. of solute, and the corresponding equilibrium temperatures, *T*, are tabulated.

(a) Solid Phase $HC_2H_3O_2$

$Sr(C_2H_3O_2)_2$, %	0.0	0.42	1.08	1.60	2.08	2.91
T	16.60	16.35	16.05	15.80	15.50	15.20
$Sr(C_2H_3O_2)_2$, %	4.31	4.82	5.73	6.06	6.52	7.15
T	14.50	14.25	13.69	13.57	13.42	13.02

(b) Solid Phase $Sr(C_2H_3O_2)_2 \cdot HC_2H_3O_2$

$Sr(C_2H_3O_2)_2$, %	4.76	4.85	4.98	5.20	5.39	5.53	5.89	6.28
T	17.0	29.7	41.5	50.5	55.5	57.3	66.5	73.8
$Sr(C_2H_3O_2)_2$, %	6.52	7.12	7.42	7.89	8.57	8.93	9.52	9.95
T	77.5	86.0	89.3	94.6	101.1	104.3	108.8	111.5

(c) Solid Phase $Sr(C_2H_3O_2)_2$ (?)

$Sr(C_2H_3O_2)_2$, %	10.45	10.76
T	118.5	121.8

The freezing point curve for this system is shown in Fig. 1. Three analyses of the solid phase (b) gave a mean value of 50.08 mole per cent.

$HC_2H_3O_2$, corresponding to the compound $Sr(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, which has not previously been reported. In the neighborhood of 113° this compound undergoes transition to another substance (c) which could not be obtained in sufficient quantity for analysis, but which appears to be unsolvated $Sr(C_2H_3O_2)_2$.

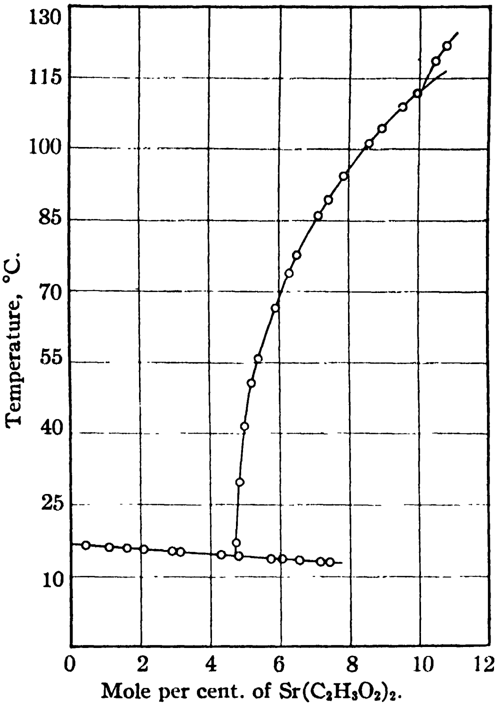

Fig. 1.—System $Sr(C_2H_3O_2)_2$–$HC_2H_3O_2$.

II. System $Ni(C_2H_3O_2)_2$–$HC_2H_3O_2$.—These solutions were green at ordinary temperatures, changing to olive-green at 115 to 120°; the most concentrated solutions were very viscous. Freezing point depression data are tabulated below.

Four solubility determinations at 30° gave values of 11.87, 13.15, 12.06 and 12.39 mole per cent., mean 12.37 mole per cent. The wide divergence among these values seems to indicate that we had here no true equilibrium between solution and crystalline solid, but that colloidal phenomena were involved. This conclusion is supported by the high viscosity of these solutions, by the marked Tyndall effect exhibited by them, and by the nature of the solid phase. This was a very finely divided greenish-white substance, which had very little tendency to redissolve in acetic acid. It showed no detectable crystalline structure upon microscopic examination, and analyses of three samples gave results varying from 54 to 66 mole per cent. of $Ni(C_2H_3O_2)_2$. This range is far in excess of any possible experimental error, and indicates that the solid is not a definite crystalline compound, but a solvated product of variable composition.

$Ni(C_2H_3O_2)_2$, %	0.0	0.32	0.61	1.00	1.73	2.47	3.22
T	16.55	16.45	16.40	16.30	16.15	16.00	15.85
$Ni(C_2H_3O_2)_2$, %	4.47	5.68	7.32	8.90	10.57	12.19	13.67	14.89
T	15.60	15.35	15.10	14.90	14.55	14.15	13.80	13.55

III. System $NH_4C_2H_3O_2$–$Ni(C_2H_3O_2)_2$–$HC_2H_3O_2$.—These solutions were green with a slight olive tinge at ordinary temperatures; at the boiling point the color was distinctly yellow-green.

At low concentrations of ammonium acetate the saturated solutions were viscous and of high nickel acetate content; in general, the solubility of the nickel compound decreased with increasing concentration of ammonium salt, but no consistent quantitative data were obtainable, nor was the solid phase even approximately constant in composition, although it always contained all three components. However, when the concentration of ammonium acetate exceeded 15 mole per cent., true equilibrium was apparently attained, concordant solubility values were found, and the solid phase appeared to be a definite compound.

The compositions of saturated solutions at 30°, in mole per cent., are

$NH_4C_2H_3O_2$, %	15.13	17.44	19.67	22.79	24.79
$Ni(C_2H_3O_2)_2$, %	0.214	0.111	0.071	0.039	0.028

The solid phase was a finely divided greenish-white substance which showed under the microscope a distinctly crystalline structure; accurate analysis was difficult because of its instability on exposure to the atmosphere. Nine analyses gave the following mean values in mole per cent.: $NH_4C_2H_3O_2$, 25.49; $Ni(C_2H_3O_2)_2$, 25.62; $HC_2H_3O_2$, 48.89. This composition was confirmed by the analysis of several wet residues; it corresponds to the compound $Ni(C_2H_3O_2)_2 \cdot NH_4C_2H_3O_2 \cdot 2HC_2H_3O_2$.

Discussion

Solubility Data.—The solubility of the monosolvate of strontium acetate in pure acetic acid at 25° was found to be 0.842 mole per 1000 g. of solvent, or 4.81 mole per cent. Comparison of this figure with the previously determined value[1b] of 0.068% for the corresponding calcium compound, and 6.40% (by extrapolation) for disolvated barium acetate,[5] shows that the solubility of these bases increases in the order of increasing atomic weight of the metal, just as in the case of the corresponding hydroxides in aqueous solution.

In the case of nickel acetate we can scarcely avoid the conclusion that the binary solutions are, at least in part, colloidal in nature. The concentration of an apparently saturated solution might then be expected to vary with particle size, conditions of stirring, temperature at which solution occurs, and other factors. Although this difficulty has not arisen in any of the previous work on acetic acid solutions in this Laboratory, phenomena of the same nature were apparently encountered by Seward and Hamblet[6] in attempting to determine the solubility of sodium iodate in this solvent, while McBain and Kistler[7] concluded that "colloidal constituents are of very common occurrence in non-aqueous solutions of electro-

(5) The solubility of a monosolvate of barium acetate at this temperature would undoubtedly be even greater than that of the disolvate. See Kendall, Davidson and Adler, THIS JOURNAL, **43**, 1489 (1921).

(6) (a) Seward and Hamblet, *ibid.*, **54**, 554 (1932). See also (b) Hill and Ricci, *ibid.*, **53**, 4305 (1931).

(7) McBain and Kistler, *J. Phys. Chem.*, **35**, 130 (1931).

lytes that are usually regarded as quite simple." This case should perhaps be regarded as parallel to the behavior of nickelous hydroxide in water. The latter compound, although known to have a crystalline structure, may, of course, be precipitated in an apparently amorphous form of variable composition (hydrous nickel oxide), and colloidal solutions of this substance are readily obtained.

Ternary solutions containing moderate concentrations of ammonium acetate show anomalies similar to those of the binary system. While the tendency toward colloidal behavior is apparently somewhat reduced by the presence of the third component,[6b] it nevertheless persists to so high a concentration of the latter as to prevent the observation of any similarity between this case and the corresponding copper system, except that at very high concentrations of ammonium acetate a solvated double salt is formed whose solubility decreases with further increase in ammonium acetate concentration. The color of the ternary nickel solutions, on heating, undergoes a pronounced reversible change toward the yellow; but since the same change occurs in similar solutions containing potassium acetate instead of ammonium, it cannot be attributed, as in the case of cupric acetate,[1c] to the formation of a complex cation containing ammonia.

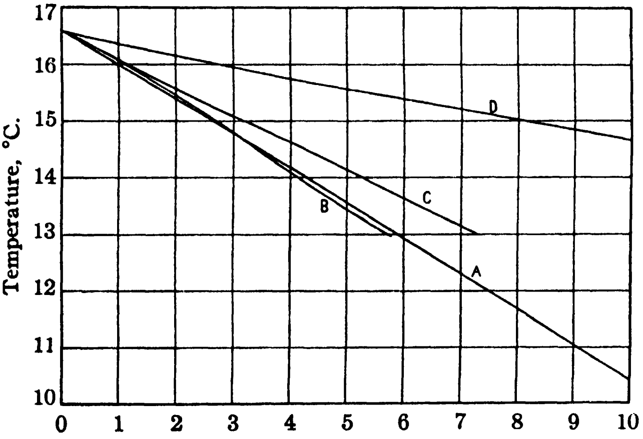

Fig. 2.—Freezing point depression curves, acetic acid as solvent: A, ideal solute; B, sodium acetate; C, strontium acetate; D, nickel acetate.

Freezing Point Depression Data.—The freezing point depression curves for the two acetates which have been studied in this work are shown in Fig. 2; for purposes of comparison we have included also the curve for sodium acetate[1a,8] and the ideal curve for a perfect *undissociated* solute. It will be noted that, in spite of the fact that all these acetates

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(8) Webb, THIS JOURNAL, 48, 2263 (1926).

are known to be ionized, and might therefore be expected to show freezing point depressions greater than the ideal values, the sodium acetate curve approaches the ideal rather closely, while the other two lie far *above* it. Now, although it is obviously impossible to determine quantitatively the molecular state of an electrolyte from freezing point data, yet valid qualitative conclusions as to the molecular complexity or type of ionization of solutes have been reached, in certain cases, by means of a simple interpretation of such data, not only for aqueous solutions, but also for such solvents as formic[9] and sulfuric[10] acids. In the case of the acetic acid solutions here considered, however, it is evident that such an interpretation might well be entirely misleading. The reason for the difficulty lies, of course, in the very low dielectric constant of acetic acid, in consequence of which interionic forces are far greater than in the other solvents mentioned, and may even become the predominant factor causing deviation from the behavior of an ideal ionized solute throughout the entire concentration range in which experimental data are obtainable. Sharply conflicting opinions as to the molecular state of simple electrolytes in acetic acid have resulted from varying interpretations of the facts just mentioned. Sodium acetate, for instance, has been regarded at one extreme as being associated to some extent into polymeric molecules,[11] at the other, as being practically completely dissociated into ions.[8,12]

Thermodynamic treatment of freezing point data, which does not demand any particular theory as to the molecular state of the solute, yields values of the mean activity coefficient of sodium acetate varying from 0.37 at $m = 0.001$ to 0.010 at $m = 1$. In the case of strontium acetate the activity coefficients cannot be determined satisfactorily, both because of the lack of data at high dilutions and because of uncertainty as to the type of dissociation of this electrolyte, but it is evident from Fig. 2 that the values must be even smaller than those for sodium acetate.

Our knowledge of acetic acid solutions is as yet scarcely adequate to permit a decision as to whether the low values of the freezing point depressions, observed even in dilute solutions of these typical electrolytes, are due to polymerization or to incomplete dissociation, or merely to the very large interionic forces prevailing in this solvent.[13] In the case of nickel acetate, however, the extremely small slope of the freezing point

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(9) Kendall, Adler and Davidson, THIS JOURNAL, **43**, 1846 (1921).

(10) Hammett and Deyrup, *ibid.*, **54**, 2724 (1932).

(11) Walden, "Molekulargrössen von Elektrolyten in nichtwässerigen Lösungsmitteln," Theodor Steinkopff, Dresden, Germany, 1923, pp. 132–135.

(12) For an intermediate viewpoint, see Hall and Werner, THIS JOURNAL, **50**, 2367 (1928).

(13) It is true that several authors [Refs. 6a, 8; also Conant and Werner, THIS JOURNAL, **52**, 4436 (1930); Hutchison and Chandlee, *ibid.*, **53**, 2887 (1931); and La Mer and Eichelberger, *ibid.*, **54**, 2763 (1932); have been fairly successful in calculating various properties of electrolytes in acetic acid on the basis of the Debye–Hückel theory and its modifications. Various arbitrary values of the parameter "*a*" are employed, however, in these calculations, as well as other hypotheses on which the several writers are not always in accord, so that experimental results may scarcely be said to have been accounted for on an entirely theoretical basis.

depression curve, as compared to that of the corresponding strontium compound, is in accord with the hypothesis advanced above that the solute is at least partially in the form of aggregates of considerably larger than molecular dimensions.

Summary

1. The solubility of strontium acetate in pure acetic acid has been determined over a wide range of temperatures, and is found to be intermediate between those of the corresponding barium and calcium salts.

2. The solubility of nickel acetate in acetic acid at 30°, as well as the composition of the solid phase in equilibrium with the solution, is found to be variable. This anomalous behavior is attributed to the presence of colloidal constituents.

3. In the presence of high concentrations of ammonium acetate, the solubility of nickel acetate is found to decrease with increasing concentration of ammonium salt.

4. Two new compounds, $Sr(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ and $Ni(C_2H_3O_2)_2 \cdot NH_4C_2H_3O_2 \cdot 2HC_2H_3O_2$, have been isolated and analyzed.

5. The freezing point depression curves of several acetates in acetic acid have been compared with the curve for an ideal solute, and their deviations therefrom have been discussed.

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Properties of Electrolytic Solutions. VI. Conductance of Sodium Triphenylstannide, Sodium Triphenylgermanide and Sodium Triphenylmethide in Liquid Ammonia[1]

BY CHARLES A. KRAUS AND W. HARLOW KAHLER[2]

I. Introduction

In the preceding paper of this series, values were given for the conductance of various salts in which nitrogen functioned as central element of the negative ion. The constitution of such ions may be modified by means of two substituent groups attached to the nitrogen atom. It seemed of interest to study corresponding ions of the elements of the fourth group, which form anions of the type R_3A^-, where R is an organic group or hydrogen. The salts of these ions are readily soluble in liquid ammonia and are appreciably soluble in ether and other similar solvents. Excepting the derivatives of tin and lead, the salts are stable in the pure state. Since an ion of this type has a very weak affinity for its charge electron, it is readily oxidized by more electronegative elements, including oxygen.

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[1] This and the preceding paper of this series formed the subject matter of the Edgar F. Smith Birthday Lecture delivered by the senior author at the University of Pennsylvania, May 23, 1930.

[2] Metcalf Fellow in Chemistry in Brown University.

The salts may be looked upon as derivatives of extremely weak acids, R_3AH, and they, therefore, react readily with most protonic solvents. Fortunately, liquid ammonia is a very weak ammonolyzing agent and solutions of these salts are usually stable in this solvent. With the exception of silicon, salts of the type of sodium triphenylmethide are not ammonolyzed under ordinary conditions.

Sodium triphenylmethide is most conveniently prepared by the action of the sodium amide upon triphenylmethane. Reaction takes place according to the equation $(C_6H_5)_3CH + NaNH_2 = (C_6H_5)_3CNa + NH_3$. A similar reaction does not take place in the case of the corresponding derivatives of silicon, germanium or tin. The alkali metal salts of triphenylgermanium and triphenyltin may be prepared by the direct action of the metal upon the corresponding free groups in liquid ammonia.

Schlenk and Marcus[3] have shown that sodium triphenylmethide is a conductor in ethereal solution. Foster[4] carried out preliminary measurements of the conductance of sodium triphenylgermanide in liquid ammonia. Wooster[5] carried out similar measurements with sodium triphenylgermanide, triphenylmethide, and triphenylstannide. These measurements indicated that salts of this type are exceptionally good electrolytes.

We have measured the conductance of these salts in liquid ammonia in the hope of obtaining data that would be sufficiently accurate to enable us to calculate their dissociation constants. Unfortunately, solutions of these salts show signs of instability at low concentrations. Of the three salts, sodium triphenylstannide proved the most stable and sodium triphenylmethide the least. From our measurements we have been able to approximate the dissociation constant of sodium triphenylstannide.

II. Apparatus and Procedure

The general procedure was much the same as that of Kraus and Hawes.[6] The solutions were made up in the conductivity cell, the materials being sealed in fragile glass bulbs which were broken as needed. The ammonia introduced into the cell was measured in a pipet, and the amount of solution withdrawn from the cell was determined by weight after evaporation and absorption in water. The conductance cell differed from that of Kraus and Hawes and is described below.

The cell consisted of a cylindrical tube A (Fig. 1), which was closed at the top by means of a ground-glass stopper through which passed the stem B, carrying the electrode system C. The stem was movable through the slip-joint D. The platinum wire leads EE (Figs. 1a and 1b) were sealed through the end of the stem and were soldered to copper wire leads passing up through the stem B. In order to render the constant of the electrodes independent of their position in the cell, they were surrounded by a housing F, which was provided with small openings GG at top and bottom to allow free flow of the solution past the electrodes. The cell was emptied by withdrawing the solution through the capillary tube H. This tube also served as stirring tube, ammonia vapor being passed through it by means of a modified Toepler pump I, similar to that used by Kraus and Hawes. Solution was withdrawn through the capillary J, which left a determinable quantity of solution in the cell. The solution passed through a special stopcock K into the receiver as described by Kraus and Hawes. Stopcocks L and M were used to equalize the pressure between the withdrawing tube and the interior of the cell.

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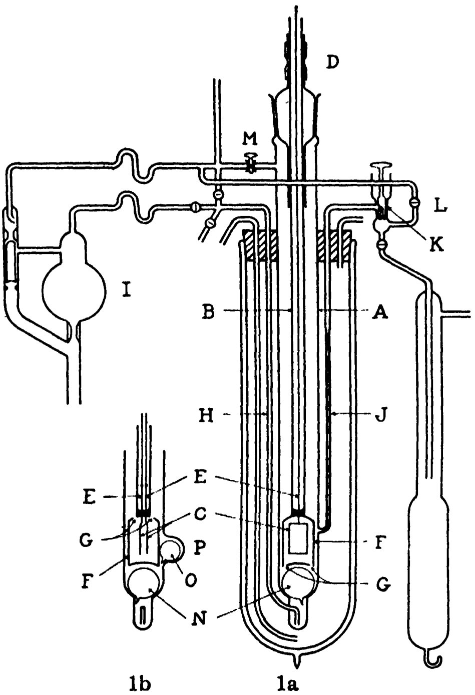
[3] Schlenk and Marcus, *Ber.*, **47**, 1678 (1914).

[4] Foster, Thesis, Brown University, 1926.

[5] Wooster, Thesis, Brown University, 1928.

[6] Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933).



1b 1a

Fig. 1.—Conductance cell.

The materials used in preparing the salts were sealed in weighed glass bulbs N and O. One of these, containing the metal, was placed immediately under the electrode housing, while the other was placed in the pocket P. The housing at the bottom was made sufficiently heavy so that the bulbs could be crushed by bearing down on the stem of the electrode system, which was movable in the slip-joint D.

After washing the cell repeatedly with liquid ammonia until the desired specific conductance was obtained, a measured quantity of ammonia was condensed in the cell, the bulbs were crushed under the liquid, and the contents of the cell were stirred. Only a few minutes were required to complete the reaction. In the case of sodium triphenylmethide, the sodium bulb was first crushed and the metal converted to amide, the reaction being accelerated by a bit of iron oxide.

The cell constant was determined by intercomparison with a standardized cell. Three different sets of electrodes were used whose constants were approximately 0.36, 0.13 and 0.06. The electrical measuring apparatus was the same as that used by Kraus and Hawes. Triphenyltin and triphenylgermanium were products that had been prepared in this Laboratory, and were purified by recrystallization from benzene. Triphenylmethane was purified by recrystallization. Sodium was introduced into weighed bulbs as described by Kraus and Hawes. Ammonia was purified as usual by means of metallic sodium. A correction of 2×10^{-7} has been applied for the conductance of the solvent.

III. Experimental Results

Conductance values of sodium triphenylstannide, sodium triphenylgermanide and sodium triphenylmethide are given in the following table. In the case of all three salts, measurements were made at concentrations much lower than the lowest given in the table. The values, however, were manifestly unreliable, since the conductance changed with time and the conductance curve showed a marked change in curvature. The difficulty was overcome to some extent by carrying the measurements out very rapidly. In the case of tin, fairly satisfactory results were obtained down to relatively low concentrations. In the case of germanium and carbon, however, satisfactory results could not be obtained at low concentrations. With sodium triphenylstannide, the conductance curve tended to rise abruptly at low concentrations, while, in the case of the triphenylmethide, the conductance curve fell consistently at concentrations below 0.001 *N*. The germanium salt exhibited an intermediate behavior. In some respects, sodium triphenylmethide behaved as though it were undergoing ammonolysis. In this connection it may be noted that, according to Kraus and Kawamura,[7] sodium triphenylmethide is completely ammonolyzed when an ammonia solution of this salt is evaporated at −33°.

TABLE I

CONDUCTANCE OF SALTS IN LIQUID AMMONIA AT −33°

V	Λ	V	Λ	V	Λ
Sodium Triphenylstannide		Sodium Triphenylgermanide		Sodium Triphenylmethide	
160.9	158.4	230.9	159.3	59.21	125.1
370.5	173.2	512.0	172.4	83.41	137.5
1146	191.3	1133	182.8	176.0	148.7
2515	202.6	2512	190.4	372.7	157.0
5520	210.7	5564	195.3	782.6	161.0
12120	214.8				
26580	218.3				
58350	219.4				

IV. Discussion

The conductance curves of the three salts are shown graphically in Fig. 2, values of the equivalent conductance being plotted as ordinates and logarithms of concentrations as abscissas. Inspection of the figure will show that all three salts are very strong electrolytes in liquid ammonia. Although the mobilities of the negative ions are relatively low because of their large size, at higher concentrations these salts are, nevertheless, much better conductors than are the ordinary salts. For the purpose of comparison, the conductance curve for sodium bromate, which is one of the stronger inorganic salts, is likewise plotted in Fig. 2. It will be noted that, although the limiting conductance of sodium bromate (278) is much higher than that of the three salts which we have measured, it is a markedly poorer conductor at concentrations above 0.01 *N*. The conductance curves for the three salts are very nearly parallel at higher concentrations, the conductance of the tin salt being highest and that of the carbon salt lowest. It was found that, toward lower concentrations, the curve for sodium triphenylmethide falls off rapidly and that of sodium triphenylgermanide less rapidly. The solutions are evidently unstable at lower concentrations. The curve for sodium triphenylstannide appears to be normal and resembles

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(7) Kraus and Kawamura, THIS JOURNAL, 45, 2756 (1923).

that of sodium triphenylboron ammide.[8] It is of interest to note that the triphenylstannide and the triphenylboron ammide ions are of about the same size and have much the same symmetry.

The determination of precise values of Λ_0 and of K is not possible, even in the case of sodium triphenylstannide. Indeed, this salt is so highly ionized that a satisfactory evaluation of K cannot be made except with highly precise data. Nevertheless, Λ_0 and K could be approximated fairly closely. The values found are: $\Lambda_0 = 226$ and $K = 0.013$. Sodium triphenylstannide is a salt having about the same strength as sodium triphenylboron ammide, and its limiting conductance has nearly the same value.

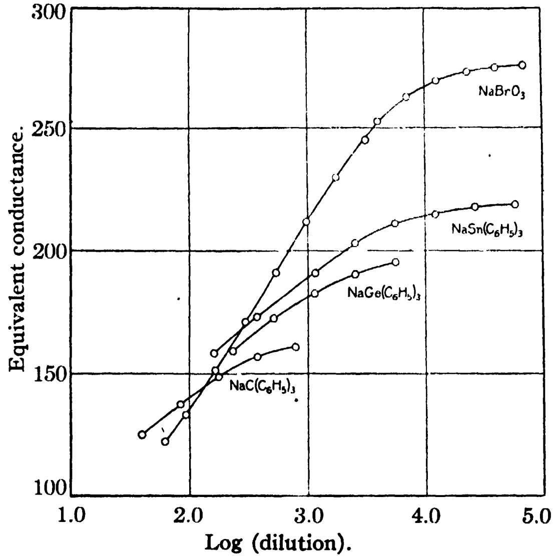

Fig. 2.—Conductance of salts in liquid ammonia.

It may be of interest to point out that familiar inorganic salts, which are usually considered to be typical electrolytes, are, in fact, much weaker electrolytes than the compounds here investigated. Thus, the dissociation constant of sodium bromate is 35×10^{-4}, while that of sodium triphenylstannide is about four times as great. The dissociation of a salt is primarily determined by the size of its ions, or, in other words, by the work necessary to separate a pair of ions from their position of minimum energy. When the ions are small, the energy of separation is large and the dissociation constant is correspondingly small.[9] It is also evident that the affinity of the negative ion for its electron has no influence on the dissociation of its salts. Thus, the affinity of an ion such as triphenylmethide or triphenylstannide for its electron is exceedingly small in comparison with that of the

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(8) Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933).

(9) Fuoss and Kraus, *ibid.*, **55**, 1019 (1933).

chloride or the bromate ion. While it is true that, in the case of the acids, ionization is the greater the more electronegative the ion, this is not true generally for salts in solvents of lower dielectric constant, where ion association is appreciable.

V. Summary

The conductances of solutions of the sodium salts of triphenyltin, triphenylgermanium and triphenylmethyl in liquid ammonia have been measured.

All three salts are very strong electrolytes. The dissociation constant of sodium triphenylstannide is approximately four times that of sodium bromate.

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Properties of Electrolytic Solutions. VII. Conductance of Sodium Trimethylstannide and of the Sodium Salts of Certain Phenols and Thiols in Liquid Ammonia

BY CHARLES A. KRAUS AND EDMUND G. JOHNSON

I. Introduction

In the two preceding papers of this series, conductance values were given for electrolytes in which the charge of the negative ion was localized on nitrogen,[1] tin, germanium or carbon,[2] the remaining valences of these elements being satisfied by organic groups. The purpose of these investigations has been to study the influence of ion size and constitution on the properties of the electrolyte, particularly its dissociation constant. The results already presented lend support to the view that the dissociation of an electrolyte is primarily determined by the size of its ions and, to a lesser degree, by their configuration. Electrolytes with large ions, which cannot approach each other very closely, have a lower energy of dissociation and, consequently, a higher dissociation constant. Where the ions are unsymmetrical, constitutional factors have a marked influence and it may be expected that the salts of such ions will be the more highly ionized the more the charge is screened by neutral atoms of the ion complex.

It seemed of interest to determine the dissociation constants of salts of simple oxygen and sulfur acids of the type RAH, which give ions of the type RA^-. The salts of the ordinary alcohols are not sufficiently soluble in liquid ammonia to permit of conductance measurements, but the salts of the aromatic alcohols are readily soluble and are well suited to the purpose of the present investigation. In the case of sulfur, both the alkyl and the aryl substituted thiols yield readily soluble salts. It was to be expected that, owing to the larger diameter of the sulfur atom, the salts of thio alcohols would prove to be markedly better electrolytes than their oxygen analogs. In the salts of alpha and beta naphthol, we have the interesting case where the oxygen atom, which presumably carries the charge electron, is located in different positions on the naphthalene nucleus, and we should expect a somewhat higher dissociation constant in the case of the α-naphtholate because of the somewhat greater screening due to the remainder of the molecule.

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[1] Kraus and Hawes, THIS JOURNAL, 55, 2776 (1933).

[2] Kraus and Kahler, *ibid.*, 55, 3537 (1933).

Sodium trimethylstannide was measured for the purpose of comparison with sodium triphenylstannide.[2] Unfortunately, this salt, like the corresponding phenyl derivative, yields solutions that are not entirely stable at low concentrations. Nevertheless, it was possible to carry out measurements to concentrations sufficiently low to show that, as was to be expected, this salt is a markedly weaker electrolyte than sodium triphenylstannide.

II. Experimental

Apparatus and Procedure.—The apparatus employed in the present investigation was very similar to that of Kraus and Kahler and need not be described, except for a few minor variations. Instead of stirring the solution by means of vapor withdrawn from the cell with a Toepler pump, the electrode system was moved up and down in the slip-joint through which the stem of the electrode system passed. An improved three-way stopcock was employed for withdrawing the ammonia, which made it possible to equalize the pressure between the cell and the withdrawal capillary without use of an additional stopcock. The electrical measuring apparatus was the same as that used by Kraus and Kahler.

Excepting sodium phenolate, all solutions were prepared by the action of sodium or sodium amide on the proper compounds in the cell itself. Sodium phenolate was prepared by the action of metallic sodium on phenol in liquid ammonia. It was washed with ether to remove traces of phenol and was sealed in weighed glass bulbs, the bulbs being broken in the cell as described by Kraus and Kahler. The naphtholates were prepared in the cell by the action of sodium amide on the corresponding naphthols. The naphtholates cannot be prepared by the action of metallic sodium on the naphthols because of the reducing action of the resulting hydrogen.[3] The thiophenolate and ethyl mercaptide were prepared by the action of sodium on the corresponding thiols. Ethyl mercaptan was introduced into the cell with a stream of ammonia vapor, a weighed bulb of sodium having been crushed under ammonia previous to introducing the mercaptan. In this case, the cell was exhausted after preparation of the salt in order to remove traces of excess mercaptan. Sodium trimethylstannide was prepared by the direct action of metallic sodium on an equivalent amount of trimethyltin in the cell.

In measuring the conductance of sodium trimethylstannide, the cell electrodes had a constant of 0.1299 and were lightly platinized. For the remaining salts, the electrodes had a constant of 4.682 and were heavily platinized.

All the solutions excepting those of sodium trimethylstannide were stable down to the lowest concentrations measured. The solutions of the sodium naphtholates were strongly fluorescent, the color being yellow by transmitted light and a deep violet by reflected light.

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[3] White and Anderson, THIS JOURNAL, 46, 965 (1924).

III. Results

The conductance values for sodium phenolate, sodium α-naphtholate, sodium β-naphtholate, sodium ethyl mercaptide, sodium thiophenolate and sodium trimethylstannide are given in Table I. The conductance values have been corrected for the conductance of the pure solvent, which was determined just prior to preparation of the solution in the case of each salt. This value *l* is given at the head of each table of values. Check measurements, made in the case of the phenolate, the α-naphtholate and trimethylstannide, were in agreement with previous values and are not tabulated.

TABLE I

CONDUCTANCE OF PHENOLATES, THIOLATES AND SODIUM TRIMETHYLSTANNIDE

V	Λ	*V*	Λ	*V*	Λ
Sodium Phenolate		Sodium β-Naphtholate		Sodium α-Naphtholate	
($l = 1 \times 10^{-7}$)		($l = 1.1 \times 10^{-7}$)		($l = 9.2 \times 10^{-8}$)	
27.41	41.22	28.23	52.71	19.19	54.20
55.03	52.19	56.74	65.07	36.93	63.46
107.8	66.05	115.8	83.19	73.11	74.41
210.9	83.48	230.3	101.1	145.6	95.16
409.3	104.2	465.1	124.8	289.8	116.2
810.0	129.1	924.3	150.3	578.0	140.5
1641	158.0	1830	177.5	1169	166.4
3280	186.7	3709	205.4	2279	192.0
6589	214.6	7419	232.3	4552	217.5
13190	239.7	Sodium Ethyl Mercaptide		Sodium Thiophenolate	
26590	257.0	($l = 8.6 \times 10^{-8}$)		($l = 9.8 \times 10^{-8}$)	
Sodium Trimethylstannide		10.67	85.08	12.11	104.8
112.1	179.5	21.46	94.84	24.31	114.9
219.2	195.7	42.75	108.5	48.98	129.1
434.0	215.9	84.57	125.9	97.20	146.2
859.1	237.7	167.3	146.9	193.1	166.0
1719	257.4	334.6	170.9	389.2	186.9
3451	274.1	667.1	195.3	767.9	207.9
		1331	218.2	1552	227.2
		2655	238.2	3118	243.3
		5320	255.4	6240	255.9

IV. Discussion

The values of Λ_0 and K for the different salts have been evaluated by the method of Fuoss and Kraus.[4] In the figure, values of the ratio Λ/Λ_0 are plotted as ordinates against the square root of concentrations as abscissas. This plot is more convenient than a plot of the conductance in comparing different salts with one another. The straight line as drawn in the figure is the limiting Debye–Hückel–Onsager slope averaged for the different salts. Actually, this slope varies slightly with Λ_0, but the variation is so small that it seemed unnecessary to introduce the limiting tangent for each electrolyte.

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(4) Fuoss and Kraus, THIS JOURNAL, 55, 476 (1933).

The curves as drawn are the calculated curves based upon the values of the constants Λ_0 and K as computed. In evaluating these constants, the following values of constants were assumed for the solvent medium: dielectric constant 22, viscosity 0.00256, temperature 240°. From the figure, it is evident that the measured values of the conductance are satisfactorily accounted for by a combination of ionic dissociation and the usual interionic effects. The deviations from the limiting Debye–Hückel slope, due to the mass action effect, is marked in all cases and is the greater, the lower the dissociation constant of the electrolyte. None of the salts are sufficiently strong to approximate the limiting curve closely.

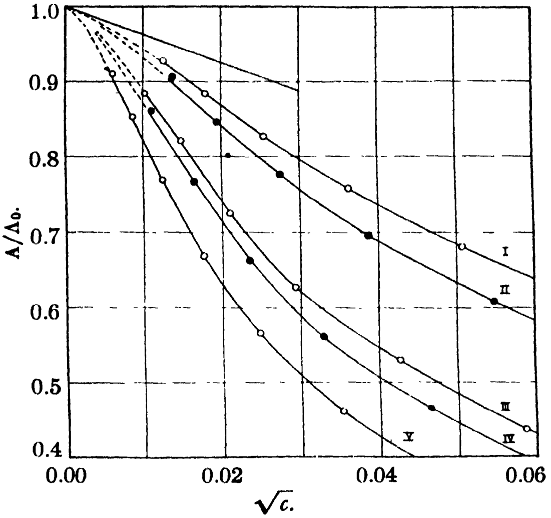

Fig. 1.—Conductance of sodium phenolates and thiolates in liquid ammonia: I, C_6H_5SNa; II, C_2H_5SNa; III, α-$C_{10}H_7ONa$; IV, β-$C_{10}H_7ONa$; V, C_6H_5ONa.

In Table II are given values of Λ_0, the limiting conductance, K, the dissociation constant, and a, which may be looked upon as the minimum distance between ion centers in the ion pairs. The quantity a was computed from the data according to the method of Fuoss and Kraus.[5]

TABLE II

CONSTANTS OF ELECTROLYTES IN LIQUID AMMONIA

Electrolyte	Λ_0	$K \times 10^4$	$a \times 10^8$
Sodium phenolate	279.4	3.82	2.70
Sodium β-naphtholate	268.1	6.50	2.94
Sodium α-naphtholate	265.3	8.08	3.08
Sodium ethylsulfide	281.4	22.5	4.04
Sodium thiophenolate	275.1	36.0	4.95
Sodium triphenylstannide	(307)	(36)	(4.95)

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(5) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

The table illustrates in striking fashion the influence of the substituent groups on the dissociation of electrolytes. Thus, the dissociation constant of sodium phenolate is 3.82×10^{-4}, while that of the β- and α-naphtholates is 6.50 and 8.08×10^{-4}, respectively. The greater size of the naphthyl group, in comparison with that of the phenyl group, has a very marked influence on the dissociation constant. It is particularly interesting to note that the dissociation constant of sodium α-naphtholate is nearly one-third greater than that of sodium β-naphtholate. This shows clearly that it is not only the size of the substituent group, but also the relation of the substituent group to the central charged atom, that determines the dissociation constant.

Sulfur, being a larger atom than oxygen, the dissociation constant of its monosubstituted ions is much greater than that of similar oxygen derivatives. Thus, sodium ethyl sulfide has a dissociation constant of 22.5, which is about three times that of the naphtholates and six times that of the phenolate. The replacement of the ethyl group by a phenyl group raises the dissociation constant from 22.4 to 36.0×10^{-4}. Sodium thiophenolate is an electrolyte as strong as the strongest of the common inorganic salts. The dissociation constant of sodium bromate, for example, is 35.0×10^{-4}.

The data for sodium trimethylstannide do not permit of an accurate determination of constants. It is believed that the values given are not substantially in error. The conductance curve of the stannide closely parallels that of the thiophenolate. The much lower value of K for the methyl derivative as compared with that of the phenyl derivative (K = 0.013, Kraus and Kahler) illustrates the influence of ion size on dissociation.

The a-values vary in accordance with the values of K. As to order of magnitude, they are in reasonable agreement with atomic dimensions. In the case of unsymmetrical ions, the a-values cannot be interpreted simply as the distance between ions; rather they represent an average distance or, perhaps better, they correspond to average energies, depending upon the relative position of the ions in the ion pair.

The results of the present investigation bring out clearly the fact that the strength of electrolytes, in solution in solvents of lower dielectric constant, varies markedly with the constitution of the ions of these electrolytes and that both the dimensions and the configuration of these ions have a marked influence upon dissociation. In general, those electrolytes will be the most highly ionized which have the largest ions and whose configuration is such that their charges are most completely screened by surrounding atoms or groups.

V. Summary

The conductance of the sodium salts of phenol, α- and β-naphthol, ethyl mercaptan, thiophenol and of trimethyltin have been measured in liquid ammonia at −33°.

Values of Λ_0 and of K have been computed and the influence of constitution upon dissociation is discussed.

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The Action of Sodium upon Trimethylgallium and Dimethylgallium Chloride in Liquid Ammonia

BY CHARLES A. KRAUS AND FRANK E. TOONDER[1]

I. Introduction

The present paper is concerned with the action of metallic sodium upon trimethylgallium and dimethylgallium chloride. In the light of our knowledge of reactions of similar derivatives of the elements of the fourth group, it might be expected that dimethylgallium chloride would be reduced to the free group $(CH_3)_2Ga$ and that this, in turn, might be further reduced to the negative ion, $(CH_3)_2Ga^-$. On the other hand, no reaction is to be expected in the case of trimethylgallium or, otherwise, a reaction in which one methyl group is substituted by the reducing metal as in the case of tetramethyltin.[2]

Excepting that free dimethylgallium $(CH_3)_2Ga$ is obtained by reduction of the corresponding chloride, there is little resemblance between reactions of organic derivatives of the elements of the third and those of the fourth group of the periodic system. Perhaps the most characteristic reaction of third group elements is that of addition of neutral molecules or negative ions, with formation of coördination compounds. Thus, in the case of boron, we have such coördinate linkage in the BF_4^- ion. Similarly, boron trifluoride combines with neutral molecules, such as ammonia or the amines, to form compounds of the type $BF_3 \cdot NH_3$.[3] There are similar compounds of the organic boron derivatives. Thus, we have $(C_6H_5)_3B \cdot NH_3$,[4] $(C_6H_5)_3B \cdot NH_2^-$,[5] and $(C_6H_5)_3B \cdot OH^-$.[6] The coördinate linkage in these compounds has a striking influence on their stability. For example, triphenylboron oxidizes in air with extreme ease, while potassium amide, under similar conditions, oxidizes explosively; yet the coördinated compound of the two is relatively stable in air.

Gallium shows much the same properties as boron in respect to the formation of coördinate linkages. Thus, trimethylgallium forms an

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(1) Du Pont Fellow in Chemistry at Brown University.

(2) Kraus and Sessions, THIS JOURNAL, 47, 2361 (1925).

(3) Kraus and E. Brown, *ibid.*, 51, 2690 (1929).

(4) Krause, *Ber.*, 57, 813 (1924).

(5) Hawes, Thesis, Brown University, 1927.

(6) Frankland, *Ann.*, 124, 130 (1862); Fowler, unpublished observations, Brown University (1933).

etherate and an ammoniate[7] and gallium trichloride forms a tetrachlorogallate ion.[8] Dimethylgallium chloride and methylgallium dichloride both form rather stable ammoniates or ammines.[8]

Trimethylgallium, when treated with sodium in liquid ammonia, undergoes a reaction in which the coördinated ammonia molecule is probably involved. Dimethylgallium chloride is reduced to the free group $(CH_3)_2$-Ga which is probably combined with ammonia. The free group reacts with additional sodium in a rather complex manner.

The methylgallium compounds are exceedingly reactive toward oxygen and many of the products of reduction are not only reactive toward oxygen and other substances but are intrinsically unstable. Accordingly, in order to arrive at some notion of the nature of the reactions involved, it has been necessary to depend largely upon indirect means. Only in exceptional cases has it been possible to separate out the products of reaction in pure form for analysis.

II. Action of Sodium upon Trimethylgallium

Weighed samples of trimethylgallium were treated with metallic sodium in liquid ammonia and the evolved gases were collected and measured. Ammonium bromide was added to the resulting solution and the gases evolved in the several stages of this reaction were collected and measured separately.

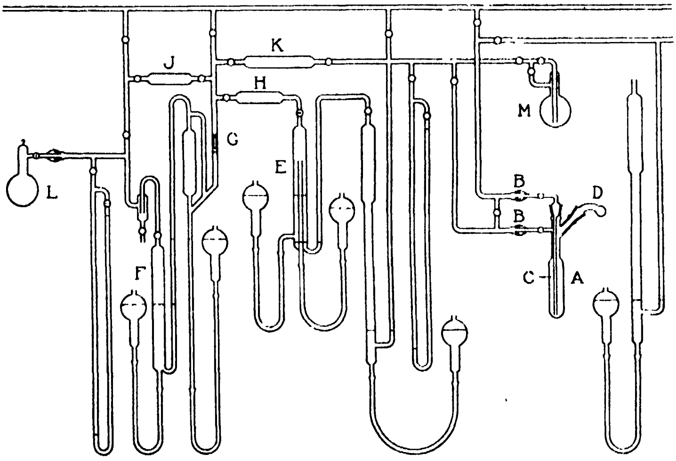

Fig. 1.—Apparatus used in reduction of trimethylgallium.

Apparatus and Procedure.—The apparatus used in this and other reactions described below is illustrated in Fig. 1. A weighed reaction tube A is attached to the system by means of de Khotinsky cement at BB. The tube is provided with a stirring tube C and an addition tube D for adding weighed quantities of substances, such as ammonium bromide, which can be formed into pellets. Gases evolved during the reaction are collected over water in E. These gases are transferred by means of a

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[7] Kraus and Toonder, *Proc. Nat. Acad.*, **19**, 292 (1933).

[8] Ref. 7, p. 298.

Toepler pump and collected over mercury in F. Water vapor and ammonia are removed by means of drying tubes H, J, K, and the density of the residual gas is determined by weighing in the calibrated density bulb L.

A weighed sample of trimethylgallium monoammine in a fragile glass bulb[7] is introduced into the reaction tube A and, after exhausting and cooling, the bulb is broken. The reaction tube is attached to the system and ammonia is condensed on the gallane, which is readily soluble. Sodium is introduced into the addition tube D previous to exhausting the reaction tube.

The Mechanism of the Reduction Process.—In several experiments known samples of trimethylgallium ammine were treated with one atomic equivalent of metallic sodium in the apparatus described above. Reaction took place immediately with evolution of hydrogen; about 0.4 atom of hydrogen per atom of gallium was evolved in the course of two hours, when reaction ceased. There was no indication of further reaction over a period of fifty hours. Ammonium bromide was then added until the characteristic blue color due to sodium was just discharged. Approximately 0.4 atom of hydrogen per atom of gallium was evolved in this stage of the reaction. On further addition of ammonium bromide to the now colorless solution, approximately 0.2 atom of hydrogen was evolved per molecule of trimethylgallium.

It is evident that several reactions are involved when trimethylgallium is treated with sodium in liquid ammonia. One of these reactions is accompanied by evolution of hydrogen while the second reaction involves some sort of a reduction process, the product of which reacts with ammonium bromide with evolution of hydrogen. Since, on completion of the reaction, approximately 40% of the sodium remains in the free state, it follows that, in one of the reactions, at least two molecules of trimethylgallium per atom of sodium are concerned. The results may be accounted for if we assume the reactions

$$\mathrm{Na} + 2(\mathrm{CH_3})_3\mathrm{Ga{\cdot}NH_3} \longrightarrow (\mathrm{CH_3})_3\mathrm{Ga{\cdot}NH_2{\cdot}Ga(CH_3)_3}^- + \mathrm{Na}^+ + {}^1/_2\mathrm{H_2} + \mathrm{NH_3} \quad (1)$$

$$2\mathrm{Na} + 2(\mathrm{CH_3})_3\mathrm{Ga{\cdot}NH_3} \longrightarrow (\mathrm{CH_3})_3\mathrm{Ga{:}Ga(CH_3)_3}^= + 2\mathrm{Na}^+ + 2\mathrm{NH_3} \quad (2)$$

In the first reaction one atom of sodium is converted to sodium amide with the evolution of hydrogen, and the amide ion forms a coördinated compound with two molecules of trimethylgallium. Reactions of this type are well known in the case of boron, although, in all known cases, only one molecule of borane combines with one amide ion.[9] The second reaction involves the direct reduction of trimethylgallium to a negative trimethylgallium ion. A compound of this type is formed when triphenylboron is treated with metallic sodium in ether solution.[10] The resulting compound, however, is highly colored. In view of the fact that the solutions, in the case of trimethylgallium, are colorless, it is probable that two trimethylgallium ions link together to form a coördinated compound.

On adding ammonium bromide to the reaction mixture, we have, first, the reaction of the ammonium ion with the metallic sodium, in which hydrogen is evolved; then, a reaction of the ammonium ion with the reduced trimethylgallium, in which hydrogen is formed and trimethylgallium is regenerated. Finally, the balance of the ammonium bromide reacts with the sodium amide complex, containing two molecules of trimethylgallium, trimethylgallium being regenerated.

Experimental Data.—A number of reactions were carried out with a view to determining the precise nature of the products of the reaction. The reaction, in general, proceeded much as described above, although the relative amounts of the substances formed in the two reactions varied measurably, depending upon conditions. In one case, where the solution was quite concentrated, one-half of an atomic equivalent of

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(9) Hawes, Thesis, Brown University, 1927; J. E. Smith, Thesis, Brown University, 1930.

(10) Krause and Polack, *Ber.*, **59**, 777 (1926).

sodium reacted according to reaction (1), and reaction (2) was entirely absent. There was introduced into the reaction tube 0.6475 g. (5.64 m. moles) of trimethylgallium and there was added 0.0844 g. (3.67 m. at.) of sodium. At the end of three hours, 31.6 cc. (2.82 m. at.) of hydrogen was evolved which corresponds precisely to one-half atom of sodium per mole of trimethylgallium. On allowing the reaction tube to stand for twenty-two hours, there was evolved an additional 4.9 cc. (0.44 m. at.) of hydrogen. This evolution of hydrogen was due to slow reaction with the solvent, sodium amide being formed. The initial reaction took place quantitatively according to equation (1). The ammonia was evaporated and the tube allowed to warm to room temperature. On exhausting the reaction tube through a liquid ammonia trap, no material collected in the trap, indicating a complete absence of trimethylgallium ammine, which sublimes readily under these conditions. Ammonia was recondensed in the reaction tube and ammonium bromide was added until the blue color due to sodium just disappeared. On further addition of ammonium bromide to the now colorless solution, no hydrogen was evolved. This indicates the absence of reaction (2).

The attempt was made to vary the proportion of reactions (1) and (2) by carrying out the reduction at lower temperatures. At −76° no reaction whatever occurred. There was a very slow reaction at −48°, accompanied by the evolution of hydrogen. At lower temperatures, both reactions proceeded so slowly that it was not practicable to carry them out. Accordingly, a reaction was carried out at −33°, using a large volume of ammonia and adding the sodium in small pieces (of about 4 milligrams each), one at a time. Of twenty pieces of sodium, seventeen had reacted at the end of six and one-half hours while the eighteenth piece required more than twelve hours for complete reaction. After collecting and determining the gases due to the initial reaction of metallic sodium, ammonium bromide was added to the now colorless solution, the hydrogen was collected and its volume and density were determined. The results were: $(CH_3)_3Ga\cdot NH_3$, 0.7330 (5.56 m. moles); H evolved, 19.0 cc. (1.70 m. at.); Na reacted (by wt.), 0.0775 (3.37 m. at.); NH_4Br added, 0.509; H evolved on adding NH_4Br, 18.4 cc. (1.64 m. at.); total H, 37.4 cc. (3.34 m. at.). According to the above data, of 3.37 m. atoms of sodium that reacted, 1.70 m. atoms reacted according to equation (1), yielding 1.70 m. atoms of hydrogen. The remaining 1.67 m. atoms of sodium reacted for the most part according to equation (2). On addition of ammonium bromide, the sodium which was combined with trimethylgallium yielded 1.64 m. atoms of hydrogen according to the equation

$$Na_2[(CH_3)_3Ga]_2 + 2NH_4Br = 2(CH_3)_3Ga\cdot NH_3 + 2NaBr + H_2$$

After completion of the last described reaction, 93% of the trimethylgallium ammine was recovered by sublimation from the reaction tube into a weighed, fragile bulb cooled in liquid ammonia.

Reaction in Ethylamine.—In the hope that reaction (1) might be absent if reduction were carried out in ethylamine solution, the reduction of trimethylgallium ammine with lithium in ethylamine solution was investigated. The reactions in ethylamine were similar to, but not identical with, those in liquid ammonia. They took place as follows

$$Li + (CH_3)_3Ga\cdot C_2H_5NH_2 \longrightarrow (CH_3)_3Ga\cdot C_2H_5NHLi + {}^1/_2H_2 \qquad (3)$$

$$2Li + 2(CH_3)_3Ga\cdot C_2H_5NH_2 \longrightarrow [(CH_3)_3Ga]_2^- + 2Li^+ + 2C_2H_5NH_2 \qquad (4)$$

The lithium, cut into small pieces, was added to a solution of trimethylgallium in ethylamine at liquid ammonia temperatures. Prior to adding the lithium, the trimethylgallium ammine was dissolved in ethylamine which was then evaporated in order to carry off the ammonia initially present. Reaction between lithium and trimethylgallium took place somewhat slowly, but, at the end of twelve hours, one atomic equivalent of lithium had reacted. The hydrogen evolved during this stage of the reaction was collected and its molecular weight and volume were determined. On distilling the ethylamine from the colorless solution, hydrogen was evolved. This hydrogen was collected and its molecular weight and density were determined. Since no ammonium bromide had been added, the hydrogen evolved during distillation of the amine must have resulted through a process of oxidation and reduction, presumably according to the reaction

$$Li_2[Ga(CH_3)_3]_2 + 2C_2H_5NH_2 \longrightarrow 2LiC_2H_5NH{\cdot}Ga(CH_3)_3 + H_2 \qquad (5)$$

The data relating to this reaction are as follows: $(CH_3)_3Ga{\cdot}NH_3$, 0.2709 (2.06 m. moles); Li, 0.0144 (2.06 m. at.); H evolved during reaction, 9.2 cc. (0.82 m. at.); H evolved during evaporation, 14.2 cc. (1.26 m. at.); total hydrogen evolved, 23.4 cc. (2.08 m. at.).

According to the above results, 39.8% of the gallium reacted according to equation (3) with evolution of hydrogen, while 61.2% reacted according to equation (4), without evolution of hydrogen. The equivalent quantity of hydrogen was, however, given off during evaporation of the solution, reaction (5) taking place. The total hydrogen, 101.0% of the theoretical, is within the limit of experimental error. While the product of reduction according to equation (3) is stable in the dry state as well as in ethylamine solution, the simultaneously formed product of reduction according to equation (4) is measurably stable only in solution at −33° and breaks down on evaporating the solvent.

On finally dissolving the product in liquid ammonia and treating with ammonium bromide, no hydrogen was evolved. This was to be expected in view of equation (5). After evaporating the liquid ammonia, the reaction tube was exhausted through a weighed trap cooled to liquid ammonia temperatures. The recovered material was obviously not the original trimethylgallium ammine, since it was liquid at ordinary temperatures and was markedly less volatile than the original ammine. One should naturally expect trimethylgallium ethylammine to be formed in this case. The weight of recovered material, which was too high for trimethylgallium ammine, would correspond to a recovery of 86% of trimethylgallium ethylammine.

Sodium bis-Trimethylgallium Ammide.—If reactions (1) and (2) express correctly what takes place when trimethylgallium is treated with sodium in liquid ammonia, then we should expect that one molecule of sodium amide would react with two molecules of trimethylgallium in liquid ammonia. Accordingly, a known quantity of sodium in a weighed, fragile bulb was introduced into the reaction tube, where the bulb was broken and the metal converted to sodium amide in the usual way. The ammonia was then evaporated and the bulb of trimethylgallium ammine, previously introduced, was broken and liquid ammonia was condensed in the reaction tube. That reaction took place was indicated by the disappearance of sodium amide, which is very slightly soluble in liquid ammonia. The solvent was now evaporated, the tube was exhausted and the product of the reaction weighed. The results were as follows: Na, 0.0497 (2.16 m. at.); $NaNH_2$, 0.0842 (2.16 m. moles); $(CH_3)_3Ga{\cdot}NH_3$, 0.5668 (4.30 m. moles); wt. product found, 0.5783 (2.15 m. moles); wt. $[(CH_3)_3Ga]_2{\cdot}NH_2Na$, calcd., 0.5775 (2.15 m. moles).

On completion of the reaction, the tube was heated to 50° and exhausted through a trap cooled in boiling ammonia. The quantity of material collected amounted to 0.0017 g., showing that the reaction between one molecule of sodium amide and two molecules of trimethylgallium was practically quantitative. On heating the product to 140° *in vacuo*, the material in the reaction tube failed to melt, although some crystals sublimed to the cooler portions of the tube. Trimethylgallium ammine melts at 30°. On cooling the tube and treating the product with ammonium bromide in liquid ammonia and thereafter exhausting the reaction tube through a trap, 48% of the original trimethylgallium ammine was recovered. Evidently some decomposition or rearrangement occurred on heating to 140°, since ordinarily the recovery amounts to 90% or more.

III. Reduction of Dimethylgallium Chloride

A. With One Atomic Equivalent of Sodium.—When dimethylgallium chloride is treated with one atomic equivalent of sodium in liquid ammonia, reduction occurs according to the equation

$$(CH_3)_2GaCl + Na = (CH_3)_2Ga + NaCl \qquad (6)$$

The free dimethylgallium combines with one or more molecules of ammonia, probably to form an ammine. When the solvent ammonia is evaporated, a brownish colored solid is precipitated, which decomposes on warming to room temperature with evolution of hydrogen according to the equation

$$(CH_3)_2Ga\cdot NH_3 = (CH_3)_2GaNH_2 + {}^1/_2H_2 \qquad (7)$$

Dimethylgallium.—Dimethylgallium chloride monoammine was prepared in a reaction tube of the type illustrated in Fig. 2a. It was attached to the system in place of the reaction tube (A) shown in Fig. 1. One atomic equivalent of sodium was introduced into the arm A, which was cut open for the purpose and then sealed. After condensing ammonia in the reaction tube, the sodium was added. Reaction took place immediately without evolution of gas and without formation of a precipitate, except that toward the end of the reaction sodium chloride appeared. The color of the solution changed gradually from yellow to orange; this color, seemingly, was due to dimethylgallium. As the liquid ammonia evaporated, a brown solid appeared and, when nearly all the liquid was gone, gas was evolved and the color of the solid changed from brown to gray. The volume and density of the gas were determined and found to correspond to one atom of hydrogen per molecule of dimethylgallium. At a temperature of 60° or above, a crystalline solid sublimed from the residue. This was later shown to be dimethylgallium amide. Equations (6) and (7) account for the products of reaction.

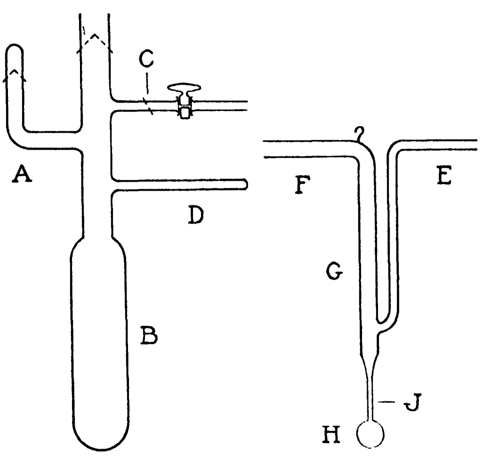

Fig. 2a. Fig. 2b.

Fig. 2.—Apparatus used in preparation of dimethylgallium amide.

In order to determine the stability of dimethylgallium, a second reaction was carried out, identical with the first, except that the ammonia was evaporated at −33°. The ammonia from the reaction tube was absorbed in sodium iodide, contained in a flask M cooled to ice temperature. In this way any evolved gases were not contaminated by air or water, nor were gases lost by absorption in water. On completion of the reaction and evaporation of the solvent, a brownish colored solid remained and no permanent gases were collected. However, on standing overnight, an appreciable quantity of hydrogen was evolved. About half the hydrogen required according to equation (7) was obtained at the end of twenty-four hours. On now warming the residue to room temperature, hydrogen was given off rapidly and the color of the solid in the reaction tube changed from brown to gray. The quantitative data were: m. moles $(CH_3)_2$-

$GaCl \cdot 2NH_3$, 5.47, 5.63; m. atoms Na added, 5.61, 5.66; m. atoms H evolved, 5.40, 5.62; ratio H/Ga, 0.987, 0.998. The dimethylgallium amide resulting from the above reactions was separated and identified.

Dimethylgallium Amide.—Since dimethylgallium amide sublimes readily in a vacuum at 100°, this compound was separated from the residue by sublimation. The material was prepared in tube B of Fig. 2a. On completion of the reaction, the tube was exhausted, filled with nitrogen, and the stopcock was sealed off at C. A Y-tube of the form shown in Fig. 2b, provided with a fragile bulb at the bottom, was weighed and arm E was attached to the pump system by means of de Khotinsky cement. Tube D of the reaction tube was cut and quickly attached to tube F (Fig. 2b) by means of a rubber slip-joint. The tube was at once evacuated and a liquid ammonia bath was placed around the Y-tube and an air-bath, heated to 100°, around the reaction tube. Dimethylgallium amide collected in arm G of the Y-tube. When a sufficient quantity had collected, the tube was heated with a small flame to melt the amide which ran into a bulb H, which was then sealed off at J. The bulb and the Y-tube were then weighed. A number of bulbs were filled in this way for analysis.

Two samples were analyzed for nitrogen and gallium. The sample bulbs were broken in an evacuated tube containing potassium hydroxide. Dimethylgallium amide dissolves slowly in water, and it was necessary to heat to 60° to effect complete solution. The ammonia formed on hydrolysis was absorbed in standard acid and titrated back with standard alkali. The gallium in the residual solution was oxidized with hydrogen peroxide and precipitated with tannin in the presence of acetic acid. A third sample was oxidized completely with sulfuric and nitric acids.

Anal. Subs., 0.2070, 0.3510: cc. of 0.09367 N H_2SO_4, 19.14, 32.24. Found: N, 12.13, 12.13. Ga_2O_3, 0.1672, 0.2647. Found: Ga, 60.09, 60.34. Subs., 0.1435: Ga_2O_3, 0.1163. Found: Ga, 60.26; mean: N, 12.13, Ga, 60.23. Calcd. for $(CH_3)_2GaNH_2$: N, 12.10, Ga, 60.21.

B. With Two Equivalents of Sodium.—A single experiment was carried out in which dimethylgallium chloride was treated with two equivalents of sodium. The first equivalent of metal reacted immediately with the formation of dimethylgallium, which formed an orange colored solution. The second equivalent yielded the familiar blue solution. In the course of twenty hours, 0.37 of an equivalent of hydrogen was evolved. On adding an equivalent of ammonium bromide, 0.54 equivalent of hydrogen was evolved, and a deep brownish-red solution resulted. When the solvent was evaporated, a brown solid was deposited, which yielded one equivalent of hydrogen on warming to room temperature. The color of the solid changed from brown to gray. The data are: m. moles $(CH_3)_2GaCl \cdot NH_3$, 3.74; m. atoms H before adding NH_4Br, 1.38; after adding NH_4Br, 1.95; after evaporation of solvent and warming, 3.74; total H, 7.08.

The total hydrogen collected was a little less than two atoms per mole of compound, which may perhaps be accounted for by loss in transferring. The first stage of the reaction proceeds according to equation (6). The excess sodium then reacts slowly with ammonia, perhaps catalyzed by the gallium compound, to form sodium amide and hydrogen. The resulting sodium amide probably combines with gallium to form a coördinated compound. On adding ammonium bromide, the excess sodium reacts to yield hydrogen, while the sodium amide is neutralized, regenerating dimethylgallium. At room temperature, this compound decomposes with evolution of hydrogen according to equation (7).

IV. Summary

The reaction of trimethylgallium ammine with sodium in liquid ammonia is in accord with the equations

$$2(CH_3)_3Ga\cdot NH_3 + Na = [(CH_3)_3Ga]_2NH_2Na + {}^1/_2H_2 + NH_3$$
$$2(CH_3)_3Ga\cdot NH_3 + 2Na = [(CH_3)_3Ga]_2Na_2 + 2NH_3$$

Depending on conditions, reaction takes place according to the first equation to the extent of from 60 to 100% of the total gallium and according to the second, from 30 to 0%. A similar reaction takes place when trimethylgallium is treated with lithium in ethylamine, except that the first reaction is replaced by the following

$$(CH_3)_3Ga\cdot C_2H_5NH_2 + Li = (CH_3)_3Ga\cdot C_2H_5NHLi + {}^1/_2H_2$$

The compound $Na_2[(CH_3)_3Ga]_2$ reacts with ammonium bromide with evolution of one atom of hydrogen per atom of sodium and the regeneration of trimethylgallium. The corresponding salt of lithium decomposes with evolution of hydrogen as the ethylamine is evaporated, lithium trimethylgallium ethyl ammide being formed.

Dimethylgallium chloride is reduced to dimethylgallium when treated with one atomic equivalent of sodium in liquid ammonia. The free dimethylgallium combines with ammonia and may be obtained as a solid at −33°, where an internal oxidation–reduction takes place slowly according to the equation $(CH_3)_2Ga\cdot NH_3 = (CH_3)_2GaNH_2 + H_2$. At room temperature the reaction is rapid. The trimethylgallium amide resulting from this reaction has been identified.

When trimethylgallium chloride is treated with two atomic equivalents of sodium, dimethylgallium is first formed, which reacts slowly with sodium presumably according to the equation $(CH_3)_2Ga\cdot NH_3 + Na = (CH_3)_2\text{-}Ga\cdot NaNH_2 + {}^1/_2H_2$. In this compound the amide ion is linked to gallium by a coördinate linkage. On neutralizing with ammonium bromide, dimethylgallium ammine is regenerated and this compound undergoes internal oxidation–reduction with evolution of hydrogen on evaporation of the solvent.

PROVIDENCE, RHODE ISLAND

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Observations upon the Ignition of Magnesium Ammonium Phosphate. VIII

BY SAMUEL J. KIEHL AND HENRY B. HARDT

There are two interesting phenomena associated with the ignition of magnesium ammonium phosphate which have been noted in the procedure for the quantitative determination of either phosphorus or magnesium. The one phenomenon is the flash which passes through the substance in the crucible during the process of ignition. The other is the dark instead of the white residue so often obtained after the ignition has been performed.

The statements in the literature as to the cause of the "flash" in the ignition of $MgNH_4PO_4$ differ widely. Possibly the one most commonly mentioned is exemplified by Karaoglanow and Dimitrow,[1] who claim that the flash is due to the presence of organic matter. They state that the flash never occurs if all organic matter is absent; they also state that incandescence will not occur if the salt is precipitated at boiling temperature, and will if precipitated at lower temperatures. They claim that the properties of $Mg_2P_2O_7$ depend upon occurrence of incandescence. Their "flashed" variety is hard, lava-like, gray to black in color, while the unflashed is amorphous, loose and quite white. Balareff[2] also obtained the two varieties but claims that moist $MgNH_4PO_4 \cdot 6H_2O$ always gives the white variety, while drying over phosphorus pentoxide for several weeks before igniting always gives black residues. He does not believe, therefore, that the gray color results from impurities, and obtains gray residues even when the precipitate has been filtered through asbestos. But in the same report he says that the gray salt examined with the microscope was seen to consist of white material containing black spots. Balareff[2] believes that the properties of the pyrophosphate obtained depend upon the degree of hydration before ignition. Popp[3] in 1870 stated that the flash was likely due to an intra-molecular change within the pyrophosphate molecule. He even accepted the theory that a change from the crystalline to the amorphous form might account for the luminescence. After reviewing and rejecting all foregoing explanations, Wöhler[4] in 1926 advanced the hypothesis that luminescence is due to a type of surface fusion or sintering. Gmelin[5] long ago believed the phenomenon to be a change from the amorphous to the crystalline form.

Since magnesium pyrophosphate is so important in quantitative analysis and in view of the many conflicting statements and opinions which have

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(1) Karaoglanow and Dimitrow, *Z. anal. Chem.*, **57**, 353 and 497 (1918).

(2) Balareff, *Z. anorg. allgem. Chem.*, **97**, 149 (1916).

(3) Popp, *Z. anorg. Chem.*, **13**, 306 (1870).

(4) Wöhler, *Kolloid Z.*, **38**, 97–111 (1926).

(5) Gmelin, "Handbuch," Vol. I, 1848, p. 107 (English Ed.).

appeared in the literature, a study of some of the properties of $MgNH_4PO_4 \cdot 6H_2O$ based upon simple experiments would be highly desirable.

Preparation of Materials.—The preparation of all salts and materials used in this investigation has been described by us previously.[6]

Apparatus.—For determining the temperature of luminescence of the salts, the apparatus shown in Fig. 1 was used. F was a long-necked, round-bottomed 100-cc. Pyrex flask which served as an air-bath. B was a bulb about 15 millimeters inside diameter, on a Pyrex tube of about 7 millimeters inside diameter. The bulb held from 0.1 to 0.2 g. when about half filled. The junction of the platinum–platinum-rhodium thermocouple, T, was in the center of the sample. The thermocouple was connected to potentiometer K, previously described by us.[6]

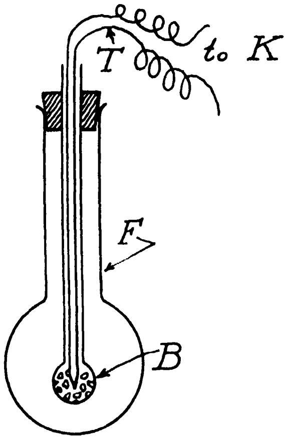

Fig. 1.

For heating the salts *in vacuo*, a thick-walled Pyrex tube 40 centimeters in length and 5 centimeters in diameter, with a ground-glass cap fitted with a stopcock, was employed. The lower third was placed in an electric furnace and the upper part was protected from the heat of the furnace by two tightly fitting asbestos sheets, so that when evacuated the lower part could be heated to above 450° while the upper end remained at room temperature. A platinum crucible containing the salt was lowered into the tube by means of a glass rod bent at the bottom into the form of a ring.

The ignitions were made in uncovered porcelain Gooch crucibles by means of either the Meker burner or an electric muffle furnace capable of maintaining a temperature of 1100°.

Experimental

TABLE I

LUMINESCENCE UPON IGNITION

	Salt	Relative intensity of flash	Temp. of flash, °C.	Nature of product
1	$MgNH_4PO_4 \cdot 6H_2O$ pptd. cold	Very strong	550–600	Snow-white, insoluble in water, volume less than half of original
2	$MgNH_4PO_4 \cdot 6H_2O$ pptd. at boiling temp.	Strong	600–615	Same as 1
3	$MgNH_4PO_4 \cdot H_2O$	Weak	600–625	Snow-white, sintered, insoluble, slightly less in vol. than original
4	$Mg_2P_2O_7$ by previously igniting $MgNH_4PO_4 \cdot 6H_2O$ at 480° in muffle	Very strong	550–600	Same as 1
5	$Mg_2P_2O_7$ by evacuating $MgNH_4PO_4 \cdot 6H_2O$ at 300°, 8 hrs.	Very strong	550–600	Same as 1
6	$MgHPO_4 \cdot 3H_2O$	Weak	550–650	Same as 3
7	$MgHPO_4 \cdot 7H_2O$	Weak	550–650	Same as 3

The $Mg_2P_2O_7$ in No. 5 above was prepared by evacuating a tube built for the purpose (described under "apparatus"), in which was placed a platinum crucible con-

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(6) Kiehl and Hardt, THIS JOURNAL, 55, 605 (1933).

taining about 5 or 6 g. of the salt. The large samples could be successively weighed, evacuated, weighed, ignited and weighed. Thus one sample of 5.9736 g. after three hours of evacuation at 300°, weighed 2.7179 g. It was ignited to constant weight over a Meker burner. The weight was then 2.7073 g. A bright flash occurred during the process. The loss in weight during the ignition over the Meker was 4 parts per 1000, and the flash was only slightly, if at all, less intense than when $MgNH_4PO_4{\cdot}6H_2O$ is ordinarily ignited.

Consequently, experiments were performed with small samples to ascertain if the material could be changed stoichiometrically to pyrophosphate before the flash occurred. The following procedure was used and the results are recorded in Table II.

A stock solution was made by placing the carefully prepared crystals of $MgNH_4PO_4{\cdot}6H_2O$ in distilled water and dissolving them by adding dilute hydrochloric acid. The concentration was determined so that 45 cc. of the solution yielded approximately 0.15 g. of magnesium pyrophosphate. For the quantitative experiments, 45 cc. of this solution was measured by a buret into a 250-cc. beaker; 50 cc. of water and six drops of magnesia mixture were then added, and precipitation effected by the addition of very dilute ammonium hydroxide at 90–100° until alkaline. After eight hours or more the precipitate was transferred to the prepared Gooch crucible and dried in an oven at 110°. This preliminary procedure was followed in all analytical experiments. Seven different samples, after the above treatment, were weighed following each successive heating in a manner indicated by captions of Table II and then flashed and finally weighed.

TABLE II

THE EFFECT OF THE FLASH ON THE WEIGHT OF $Mg_2P_2O_7$

After heating one hour at 480°, g.	After 8 hours more at 480°, g.	After the flash, g.	After heating 1.5 hours at 925°, g.
0.1481	0.1480	0.1478	0.1478
.1476	.1473	.1471	.1473
.1478	.1480	.1478	.1479
.1480	.1481	.1478	.1479
.1482	.1482	.1480	.1480
.1474	.1474	.1474	.1473
.1479	.1479	.1478	.1478

The data in Table II indicate that conversion to the pyrophosphate was complete before the flash occurred.

Another interesting fact was learned in the flash. Our system rose in temperature at least fifty degrees during the change with samples of one-tenth of a gram. Heat was evolved. A substance of greater stability was without doubt formed. The substance also before the flash was quite soluble in acids while the final residue after the flash, as is commonly known, was difficultly soluble.

Moreover, when any of the hydrates of $MgNH_4PO_4$ or $MgHPO_4$ were converted to the pyrophosphate by heating below 500° and the residues examined with the microscope, it was found that the shapes of the original crystals had been retained. They were, however, always opaque. During the flash this shape disappeared entirely. But it was suspected, however, that the opaque crystal-shaped particles were amorphous because they were opaque and that since a large amount of energy was liberated in the transformation, the final amorphous-looking material might be crystalline.

In attempting to answer the questions thus raised, x-ray diffraction pattern photographs of samples of the salts in question were made. These photographs show in Fig. 2 very definite crystal patterns for 1, $MgNH_4PO_4 \cdot 6H_2O$; 2, $MgNH_4PO_4 \cdot H_2O$; and 4, the residue ($Mg_2P_2O_7$) after the flash from either $MgNH_4PO_4 \cdot 6H_2O$ or $MgNH_4PO_4 \cdot H_2O$. But 3, the unflashed pyrophosphate from either $MgNH_4PO_4 \cdot 6H_2O$ or $MgNH_4PO_4 \cdot H_2O$, shows no pattern and is therefore not crystalline. Samples of $Mg_2P_2O_7$ fused in an oxy-gas flame or heated in a muffle at 1000° for ten hours gave patterns identical with 4. The form thus obtained is no doubt the stable form.

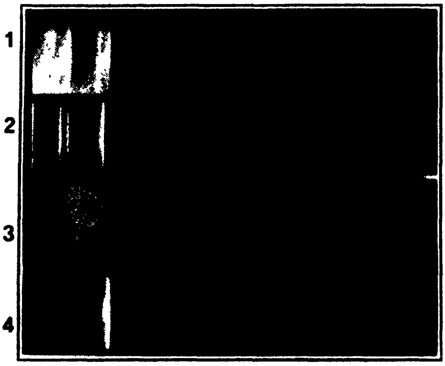

Fig. 2.

The Dark Residue.—$MgNH_4PO_4 \cdot 6H_2O$ possesses the very striking and interesting property of attaching firmly certain types of organic compounds while it is losing water of hydration and ammonia. When $MgNH_4PO_4 \cdot 6H_2O$ was heated in an open platinum crucible without contact with organic materials, it invariably gave a white residue, but in an atmosphere of certain gaseous organic compounds a black residue always resulted. Stearic acid wetting the end of a stirring rod which was held in the crucible above the salt—not touching it—while it was gently heated produced a black residue. Glycerin and paraffin treated similarly gave the black residue. A bit of filter paper placed upon the bottom of the platinum crucible with the salt on the other side out of contact produced gaseous products when it was gently heated and caused the formation of a black residue. A gentle stream of unignited commercial gas used as fuel in our laboratory—an ordinary commercial water gas enriched with illuminants—was directed upon the salt during the gentle heating. A black residue was left. In preparing the furnace for a long period of service at 250°, a clean strip of asbestos paper was placed in the bottom. The salt upon a clean watch glass which was covered with a larger one held by glass supports was placed in the furnace set for 250°. After one hour the salt was a dirty brown from the vapors given off, probably by the binder used in the asbestos paper. This material even after heating at 250° for days and final ignition over the Meker burner could not be freed from this coloration. A strip of the same asbestos paper 6.3 mm. wide and 5.1 cm. long placed across the top of the uncovered crucible invariably caused a brown-black residue to be formed when it was gently heated. The following liquids left the residue white when employed as above: benzene, carbon tetrachloride and chloroform. None of the following gases produced a coloration of the residue: hydrogen, acetylene, carbon dioxide, carbon monoxide, or air. On the other hand, the same treatment was applied to the magnesium ammonium phosphate monohydrate and the residue was white or under the severest test but a very light gray. When the $MgNH_4PO_4 \cdot 6H_2O$ was boiled with absolute alcohol, five molecules of alcohol substituted for five molecules of water. Ether also will displace some of the water.

It seems therefore that the hexahydrate during the process of losing water of hydration possesses an extraordinary capacity for firmly attaching certain types of carbon compounds, which decompose upon heating to higher temperatures and leave graphitic carbon.

Discussion

The x-ray photographs furnish the evidence that the two original salts are crystalline substances, that the unflashed but converted pyrophosphate from both sources is amorphous, and that the flashed pyrophosphates from both sources are identical in crystalline form.

The flash is therefore caused by the sudden heating of the material to incandescence when the energy is released upon crystallization of an amorphous substance. J. Böhm[7] has reported a similar behavior for other substances. The melting point of the substance, 1383°, together with its optical properties have been reported by Olaf Anderson.[8]

An amorphous substance is a supercooled liquid and is metastable. It should, upon crystallization, liberate energy. It should be more soluble. That the crystallization should occur rapidly between 500 and 650° for these substances is not strange. The melting point is 1383°, and below this the velocity of transition would gradually increase and reach a maximum which might be somewhere between 500 and 650°, then recede as is the case with many other substances. In this case a very rapid evolution of heat raises the temperature of the substance to incandescence. In fact, by holding the materials for a considerable time at a little over 500°, the crystalline form has been prepared from the amorphous less quickly and without the flash.

The dark colored residue from our experiments is caused by the adsorption of gaseous carbon compounds such as would result from the destructive distillation of cellulose. With carefully purified materials and in an atmosphere free from such compounds, a snow-white residue results. With gentle ignition of the hexahydrate in an atmosphere charged with gaseous products from charring filter paper, stearic acid, glycerin and some other substances, the black residue forms.

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(7) Böhm, *Z. anorg. allgem. Chem.*, **149**, 217 (1925).

(8) Olaf Anderson, *J. Wash. Acad. Sci.*, **4**, 318 (1914).

The monohydrate does not possess this property to any degree comparable to the hexahydrate. But very light gray colored residues were produced under circumstances which produced the black residues with the hexahydrate.

It seems reasonable, therefore, that a substitution of these gaseous carbon compounds might be made for the water in the structure of complex hexahydrate. Higher temperatures would cause the firmly bound carbon compound to decompose and leave graphitic carbon which, upon further ignition, is extremely difficult to oxidize.

The authors wish to acknowledge their indebtedness to Professor Paul F. Kerr of the Department of Geology, Columbia University, for the x-ray work which appears in this paper.

Summary

1. The luminescence or flash during the ignition of magnesium ammonium phosphate hexahydrate and of magnesium ammonium phosphate monohydrate is due to the rise of temperature caused by the large quantity of heat liberated when the amorphous form of $Mg_2P_2O_7$ crystallizes.

2. The magnesium ammonium phosphate hexahydrate during the process of losing water of hydration in the early stages of ignition possesses the property of attaching firmly within its complex structure certain gaseous organic compounds, if present, which later break down and leave graphitic carbon.

NEW YORK CITY

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Sorption of Organic Vapors by Resinous and Cellulosic Materials

BY CLARENCE H. WINNING AND JOHN WARREN WILLIAMS

The objects of a recent sorption balance study of the behavior of glyceryl phthalate resins in the presence of acetone and methyl alcohol vapors were stated to be five-fold: (1) to determine the form of the sorption isotherms at several temperatures and to interpret the curves in terms of the porous structure of the resin; (2) to determine the heat of the sorption processes by the comparison of two isotherms; (3) to make an estimate of the average pore size from the sorption behavior in the neighborhood of saturation; (4) to study the changes in structure produced by variations in the curing process to which the resin has been subjected; (5) to study the reversibility of the sorption process. The results of this study[1] were so interesting that it was decided to extend the work to other artificial resins, to several natural resins and to certain derivatives of cellulose, using the vapors of ethyl ether and chloroform as sorbate molecules.

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[1] Winning and Williams, *J. Phys. Chem.*, **36**, 2915 (1932).

The apparatus used was a McBain–Bakr balance, adapted to the sorption of vapors by powdered resin samples. It is completely described in the earlier article. Except for insignificant details the experimental procedure used was the same as that already described. Its particular advantage lies in the fact that it permits a continuous and complete sorption and desorption experiment to be made without disturbing the sorbent in any way, both with respect to the equilibria attained at the several partial pressures and to the rate at which these equilibrium values are approached. At the same time any effects of a true hysteresis will probably be recognized as readily by this method as by any other of procedure. The time allowed for the attainment of equilibrium was extended in certain cases to two full days; in the majority of cases, however, less time was required.

Experimental

Materials Used.—The glyptal resin spoken of in this article was prepared from glycerin and phthalic anhydride according to directions previously given. It was not "cured," and would therefore correspond to what has been called Resin I in the earlier article.

Phenolphthalein benzoate resin was prepared following the directions recently given by Zelinsky and Maksorow.[2]

A method of Lilienfeld[3] was used in the preparation of the benzyl cellulose. The material was heated in an evacuated tube for two days at 160° to remove absorbed liquid.

The cellulose acetate material was prepared by an acetylation process which results in a complete solution of the product.

As samples of natural products resins described as Pontianic Borneo and Congo fossil were used.

The organic liquids used, chloroform and ether, were subjected to rigorous purifications before being sealed into the sorption chambers.

TABLE I(a)

DATA FOR 35° ISOTHERMS—CHLOROFORM VAPOR

	Amounts sorbed per gram (x/m)			
p_x/p_s	Glyptal	Phenolphthalein benzoate	Benzyl cellulose	Cellulose acetate
0.202	0.243	0.151	0.088	0.176
.334	...	.163	.132	.239
.508	...	.381	.212	.367
.662	.257	.723	.331	.504
.817	.418	...	...	.765
.838	...	1.545	.914	...
.614	.350	0.585	.301	.563
.202	.310	.234	.097	.250

TABLE I(b)

DATA FOR 50° ISOTHERMS—CHLOROFORM VAPOR

	Amounts sorbed per gram (x/m)			
p_x/p_s	Glyptal	Phenolphthalein benzoate	Benzyl cellulose	Cellulose acetate
0.116	0.003	0.033	0.051	0.074
.191	.008	.046	.067	.109
.318	.024	.080	.100	.173
.468	.080	.227	.160	.270
.668	.133	.677	.292	.436
.845	.394	1.432	.848	.737
.572	.295	0.473	.244	.463
.265	.270	.214	.107	.256
.116	.253	.168	.060	.154
.000	...	...	.000	.007

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(2) Zelinsky and Maksorow, *Ind. Eng. Chem.*, **24**, 63 (1932).

(3) Lilienfeld, U. S. Pat. 1,858,019.

TABLE II

DATA FOR 35° ISOTHERMS—ETHER VAPOR

	Amounts sorbed per gram (x/m)			Amounts sorbed per gram (x/m)	
p_x/p_s	Congo fossil	Pontianic Borneo	p_x/p_s	Congo fossil	Pontianic Borneo
0.238	0.036	0.029	0.935	0.810	0.705
.326	.056	.056	.693	.218	.210
.450	.063	.080	.498	.132	.131
.572	.102	.117	.361	.100	.092
.693	.221	.210	.238	.083	...

Data and Results.—The results of representative experiments are presented in the form of tables and graphs.

Discussion

The Sorption and Desorption Processes.—High molecular weight substances of the type considered in this article are frequently assumed to have practically no permanent interspaces within the structural framework. They should then take up vapors by processes other than condensation unless these adsorption processes result in a partial resolution into the constituent molecules. The sorption curves for acetone and methyl alcohol on glyptal could be divided into three parts. In the first of these regions the highly polar sorbate molecules were able gradually to overcome strong cohesive forces, thereby penetrating the structure. Once the sorbate molecules have penetrated the structure the equilibrium value for the amount adsorbed is attained more readily and the isotherm becomes parallel to the pressure axis, indicating the completion of a process which we have assumed to be the filming of the structural units. As the partial pressure of the sorbate is further increased, a limited swelling takes place and the capillary spaces formed become filled with condensed liquid. Thus the process of adsorption is followed by one of condensation within the pores which have been opened up.

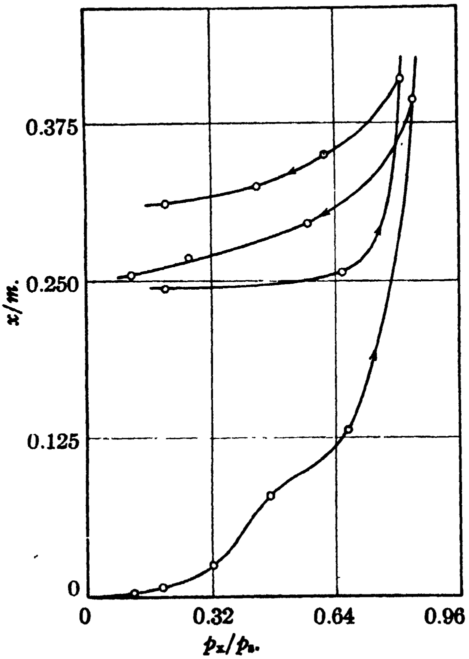

Fig. 1.—Glyptal-chloroform, 35 and 50° isotherms.

In the extension of the work to other sorbents and to other sorbate materials it was found that no two of the systems behaved exactly alike, yet in certain cases marked similarities in sorption and desorption curves were evident. A sample of "uncured" glyptal resin was found to take up chloroform vapor less readily than either acetone or methyl alcohol at the lower vapor pressures, but the three sorption regions described above are again recognizable in the 50° isotherm (Table I, Fig. 1). The adsorption process is an exceedingly slow one. This is probably to be accounted for on the basis of a closely knit structure which makes the inner surface areas difficultly accessible to the vapors of a larger molecule like chloroform, for it is believed that our experimental conditions preclude the necessity of a displacement of strongly adsorbed gases from the surfaces. The desorption process is irreversible to a marked extent, even far into the so-called condensation region. It is difficult to account for the tenacity with which the chloroform vapors are held, especially in the region where large amounts of vapor have been taken up and the uncured glyptal has assumed the appearance of a semi-fluid mass. A restrained diffusion would seem to furnish the most likely explanation, in which case experiments over much greater periods of time would undoubtedly improve the situation.

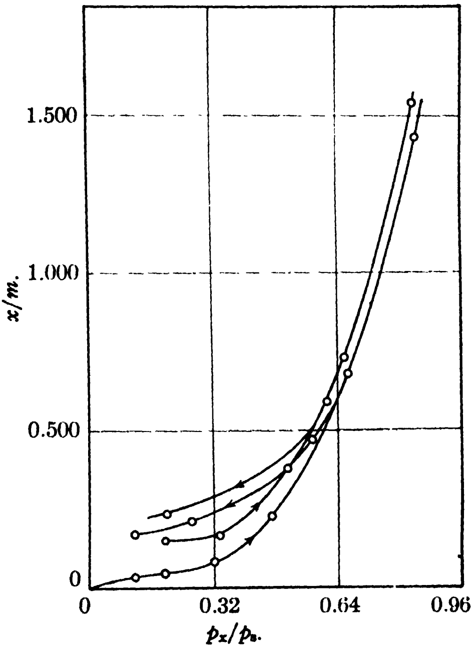

Fig. 2.—Phenolphthalein benzoate-chloroform, 35 and 50° isotherms.

The phenolphthalein benzoate resin, one of a series of phenolphthalein resins prepared by Zelinsky and Maksorow, was chosen as typical of a substance believed to have properties intermediate between the amorphous resins and those materials which are characterized by some regularity in structure. It takes up chloroform vapor in a normal way (Table I, Fig. 2), the sorption isotherm having the typical "S" shape which is so characteristic of a swelling gel. After completion of the 50° isotherm the same sample was used for experiments at 35°. It will be observed that at this temperature the sample did not begin to increase in weight until a partial pressure of 0.3 was reached.

The chloroform sorption and desorption data for the benzyl cellulose resin (Table I, Fig. 3) are interesting because of their resemblance to those which are presented for cellulose acetate using chloroform as sorbate (Table I, Fig. 4), and to those which have already been considered in the earlier article where acetone and methyl alcohol vapors were taken up by this ester. In all these cases closed sorption and desorption cycles are established. However, the hysteresis is much less marked with benzyl cellulose and it is possible to construct an equilibrium curve by interpolation, from which certain thermodynamical calculations seem justified. In this way information with regard to the sorption process in the region of the higher partial pressures for substances of cellulosic nature may be obtained. It should also be pointed out that the benzyl cellulose is much more readily disintegrated by chloroform vapors than is cellulose acetate. In this respect the ether is similar to an uncured glyptal. It is generally true that the sorption and desorption processes approach apparent equilibrium at a more rapid rate in the case of the cellulosic materials studied than is the case with the resins.

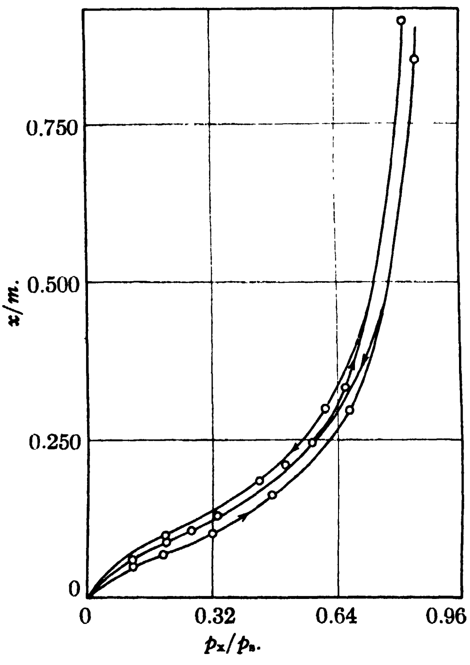

Fig. 3.—Benzyl cellulose-chloroform, 35 and 50° isotherms.

The sorption of ether vapor by the natural resins (Table II, Fig. 5) closely resembles that of acetone by cured glyptal resins. This resemblance suggests a similarity in structure. These natural resins are fossilized or aged to different degrees. The more mature resin (Pontianic Borneo) offers the greater resistance to the penetration of the vapors in the region of low partial pressures, presumably because of a more compact structure. The sorption and desorption processes are completely reversible in the higher partial pressure areas.

Irreversibility of the Sorption.—In no system investigated did we find the sorption and desorption processes to be completely reversible. In certain cases they approached reversibility when the partial pressures corresponded to the "capillary condensation" region. But if one subjects a sample of uncured glyptal resin to the action of chloroform vapor, the sorption and desorption processes are not at all reversible, even in the region of extremely high partial pressures. This will be evident from an inspection of Fig. 1. The 35° isotherm was determined using the same sample that had been used previously at 50°. Reduction in partial pressure for a period of several days did not serve to lower the vapor content to any appreciable extent.

On the basis of the hysteresis behavior, the substances studied may be divided into two classes, those which give a closed hysteresis cycle and those which apparently do not return to their original condition no matter how rigorous the evacuation treatment. Of the substances investigated, glyptal, phenolphthalein benzoate, and the natural resins did not return to their original weight. In agreement with Urquhart,[4] with Sheppard and Newsome[5] and with others who have studied the sorption of water vapor by cellulose derivatives, these materials were found to complete a cycle upon desorption whether acetone, methyl alcohol, or chloroform vapors were used in the experiments. The hysteresis cannot be entirely accounted for on the basis of the theory of the curvature of the liquid meniscus in the capillary spaces,[6] nor does its explanation on the basis of an interference of air or water with the wetting and filling of the pores seem satisfactory. It must be bound up in some way with the interaction between the active parts of the surface of the structural units and the molecules approaching these surfaces.

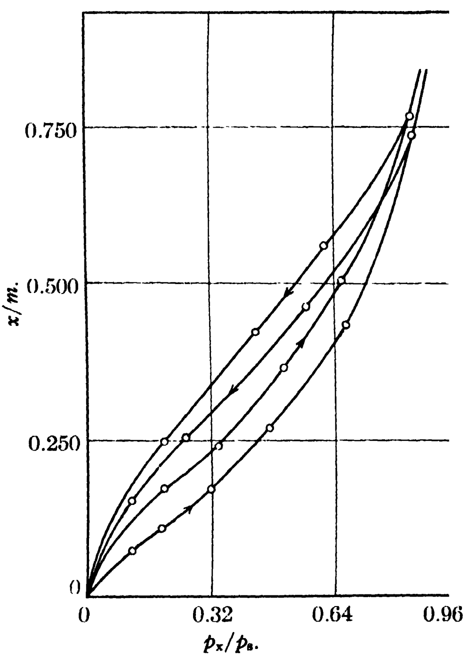

Fig. 4.—Cellulose acetate–chloroform, 35 and 50° isotherms.

The difference between the closed cycle type of hysteresis (cellulose derivatives) and that in which the desorption process fails to reduce the amount of vapor adsorbed to extremely small quantities at the very low partial pressures seems to be a real one, probably to be explained in terms of a difference in the forces which bind the liquid to the solid. Thus, while it was not considered safe to resort to an interpolation process to locate equilibrium curves for thermodynamic calculations in the case of the cellulose acetate, such a treatment has proved quite satisfactory in the

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(4) Urquhart, *J. Textile Inst.*, **20**, 125T (1929).

(5) Sheppard and Newsome, *J. Phys. Chem.*, **33**, 1817 (1929).

(6) See, for example, Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

case of the glyptal,[1] phenolphthalein benzoate and natural resins. The data for the benzyl cellulose sorption could be treated in this manner only because the area of the hysteresis cycle was small. Such a procedure is not without real experimental justification in the case of the resins because desorption experiments carried out over very greatly extended periods of time decrease the observed hysteresis to a certain extent. This is clearly indicated by the arrow in Fig. 3 of the earlier article. Usually the hysteresis area does not extend far into the region of capillary condensation; furthermore, it is greatest at the infinitely small vapor pressures.

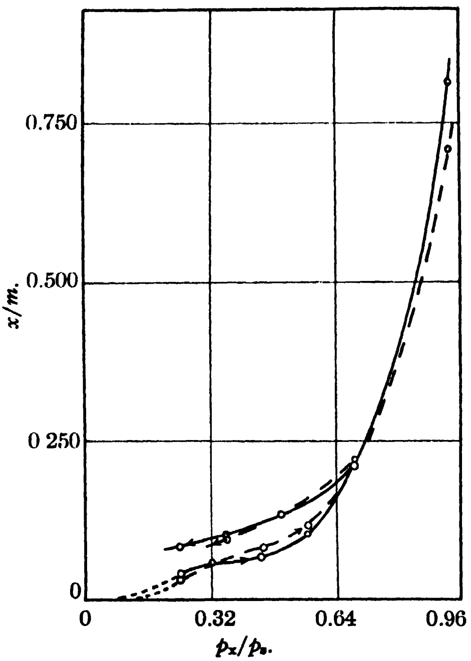

Fig. 5.—Ether vapor, 35° isotherms: Congo fossil———; Pontianic Borneo— — —.

A tentative explanation for the difference in the two kinds of hysteresis may be suggested if it can be assumed that the build of a gel material of the type considered in this article is predetermined by molecular orientations in the solution form. In general it seems safe to consider that elongated and regularly shaped units in the sol form may lead to the formation of an orderly and sensibly reproducible structural arrangement in the gel form, while odd-shaped molecules may be expected to give rise to accidental packings as the gel is again formed. The swelling of a gel may be explained by saying that either the forces holding the micelles together to form the massive material, or the forces causing the aggregation of molecules (or both, as the case may be), are overcome as the sorbate is able to penetrate more and more deeply. The sorption process is described as one in which first the structural units (molecules) are filmed, and then a condensation takes place in the voids or capillaries formed by the continued penetration of the sorbate. There is, therefore, a definite tendency toward a solution process. As the sorbate is removed from a system the reassociation of molecules may be such as to permit its eventual complete removal if the arrangement is a regular, and, as it was in the cases investigated by us, a less closely knit one; or it may be such as to effectively block and trap relatively large amounts of the sorbate due to random arrangements of molecules which may have different sizes as well as irregular shapes. Also, it is a recognized fact that in the study of the energetics of the sorption processes the distances between adsorbing surfaces and sorbate molecules are of fundamental significance in determining the relative importance of the adhesive and cohesive forces which result. A regular arrangement would seem to favor cohesion between adsorbing surfaces while in a random arrangement the adhesive forces could not be so completely overcome because the distance between adsorptive surfaces would always be variable, thus preventing practical return to the vapor-free or original state. Experiments designed to test this suggestion are now being made.

Thermodynamics of the Sorption Process.—Another of the methods by which there may be made available information with regard to the sorption processes at the solid–vapor interface is a study of the heats of the sorption. Provided the assumption can be made that the available solid surface remains constant in area during the adsorption, the affinity of such a surface which already contains the amount x of adsorbed vapor for the molecules of the vapor is

$$-\Delta F = RT \ln (p_s/p_x)$$

The total heat of wetting, $-\Delta H$, may therefore be determined using the Gibbs–Helmholtz equation

$$\Delta H = \Delta F - T\,(\partial \Delta F/\partial T)_x$$

Performing the operation indicated and integrating

$$-\Delta H = \frac{2.3\ RT_1T_2}{T_2 - T_1}\left(\log \frac{p_{x2}}{p_{x1}} - \log \frac{p_{s2}}{p_{s1}}\right)_x = -\Delta H_1 + \Delta H_2$$

The first term on the right side of this equation is the differential heat of adsorption and the second term, which is independent of the amount adsorbed, is the heat of vaporization of the liquid being condensed in the capillaries.

At low values of partial pressure the magnitudes of $-\Delta H$, and therefore of the differential heats of adsorption, may be very high. Our data are sufficient to show that as the amount of vapor adsorbed becomes greater $-\Delta H$ approaches zero because the value for the differential heat of adsorption approaches that of the latent heat of vaporization of the liquid being taken up by the solid material. This is shown by the data which have been collected to form Table III. The latent heat of vaporization for chloroform at its boiling point is 58.8 calories per gram.[7] The value calculated to 42.5° will be slightly more than 3 calories larger, or approximately 62 calories. The last column of both parts of Table III indicates a differential heat of adsorption which is only slightly larger than this value, suggesting that after the adsorption on the surface of the structural units of the materials has been completed the gel structure is opened up by a limited swelling and a condensation of the vapor takes place in the capillaries formed in this manner.[8] These data may therefore be considered to

(7) Mathews, THIS JOURNAL, 48, 562 (1926).

(8) Peirce, *J. Textile Inst.*, 20, T133 (1929).

indicate the importance of the process of condensation to liquid in the region of higher partial pressures.

TABLE III(a)[a]

CHANGE IN HEAT CONTENT DURING SORPTION PROCESS. BENZYL CELLULOSE RESIN—CHLOROFORM VAPOR

Calculations Made from Equilibrium Curves Determined by Interpolation

x/m	p_x/p_s (35°)	p_x (35°), mm.	p_x/p_s (50°)	p_x (50°), mm.	$-\Delta H_1/g.$
0.100	0.223	67.2	0.278	146.2	86.3
.150	.368	110.9	.420	221.0	76.5
.300	.620	186.8	.660	347.2	68.8
.450	.715	215.4	.757	398.2	68.2
.600	.762	229.6	.805	423.4	67.9
.750	.794	239.2	.836	439.7	67.6
.900	.816	245.9	.854	449.2	66.9

TABLE III(b)

CHANGE IN HEAT CONTENT DURING SORPTION PROCESS. PHENOLPHTHALEIN BENZOATE RESIN—CHLOROFORM VAPOR

Calculations Made from Equilibrium Curves Determined by Interpolation

x/m	p_x/p_s (35°)	p_x (35°), mm.	p_x/p_s (50°)	p_x (50°), mm.	$-\Delta H_1/g.$
0.300	0.428	129.0	0.458	240.9	69.3
.450	.547	164.8	.574	301.9	67.2
.600	.614	185.0	.643	338.2	66.9
.900	.712	214.5	.743	390.8	66.6
1.200	.782	235.6	.812	427.1	66.0
1.500	.832	250.7	.858	451.3	65.2

[a] These tables contain data which are entirely analogous to those of Table V of the previous article [Winning and Williams, *J. Phys. Chem.*, **36**, 2915 (1932)]. The data of the last column of this Table V are values calculated per gram of sorbent; therefore the word "mol" was inadvertently inserted.

The authors desire to express their appreciation to the Research Committee of the University of Wisconsin for substantial aid.

Summary

1. A balance of the McBain-Bakr type has been used to study the sorption of chloroform vapor by samples of glyptal, phenolphthalein benzoate, benzyl cellulose and cellulose acetate maintained at 35 and 50°. The sorption of ether vapor by samples of two natural resins maintained at 35° has also been investigated.

2. The sorbent materials may be characterized as typical swelling gels. As vapors continue to be taken up by them, the first process of surface adsorption is followed by a physical process of condensation of sorbate in capillary spaces or voids. These capillaries have been opened up after the structural units, probably molecules, have been completely filmed.

3. The hysteresis behavior of the resinous materials is different from that of the two cellulose derivates. An attempt is made to account for this difference on the basis of structural considerations. Regular

arrangement in build is believed to favor practically complete removal of sorbed vapors at extremely low partial pressures while random arrangement may lead to conditions which result in retention.

4. The heats of the several sorption processes have been calculated from the free energy changes, and their temperature coefficients.

MADISON, WISCONSIN RECEIVED APRIL 25, 1933
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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Potential of the Silver-Silver Iodate Electrode at 25°

BY J. N. PEARCE AND VERDA I. WIRTH

Any slightly soluble salt of a metal may form, potentially, a good electrode, provided the electrode is perfectly reversible and the metallic salt is stable in solution. The present paper gives briefly the results obtained from a study of the silver-silver iodate electrode.

Materials and Apparatus.—The silver crystals used in the preparation of the electrodes were formed by the electrolysis of a hot, concentrated solution of pure silver nitrate, using a platinum wire cathode and a pure silver anode, surrounded by a porous cup. A current of five to ten amperes gave uniform, well-defined crystals which were free from amorphous silver.

Silver iodate was prepared by adding a dilute solution of pure silver nitrate slowly and with rapid stirring to a large volume of a dilute solution of potassium iodate. The precipitate was washed free from excess salts and dissolved in a pure concentrated solution of ammonium hydroxide. The ammonia was allowed to evaporate spontaneously, leaving the iodate in the form of fine white crystals.[1] These were washed thoroughly and stored under conductivity water until used.

All other chemicals were carefully purified by approved methods. All solutions were made on the weight molal basis in conductivity water.

The experimental data recorded in the following tables are the mean potential values obtained from three to five cells, each containing three to five individual electrodes. While the calomel electrodes attained equilibrium quickly, the iodate electrodes required four or five days. The deviations of the potentials of the different electrodes in any single iodate half-cell did not exceed 0.05 mv., and the mean deviation of duplicate half-cells containing potassium iodate did not in any case exceed 0.2 mv.

The determination of the potentials of the iodate electrodes involved the measurement of electromotive forces of cells, with ion transference, of the type: Hg, Hg_2Cl_2, KCl (0.1 *m*), KIO_3 (0.1 *m*), $AgIO_3$, Ag. The half-cells were connected by a modified form of the Lamb and Larson[2] flowing junction device. The liquid junction potentials were calculated by means of the relation used by Lewis and Sargent,[3] namely

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[1] Greensfelder and Latimer, THIS JOURNAL, **53**, 3813 (1931).

[2] Lamb and Larson, *ibid.*, **42**, 239 (1920).

[3] Lewis and Sargent, *ibid.*, **31**, 363 (1909).

$$E_l = RT/nF \ln \lambda_1/\lambda_2$$

where λ_1 and λ_2 are the equivalent conductances of the chloride and iodate solutions at the same concentrations, respectively. This potential must be added to the potential of the cell with ion transference, E_t, to give the potential of the cell, E, without ion transference. Since data on the conductance of potassium iodate solutions[4] at 18° only are available, we have made the assumption that the ratio of the equivalent conductances of the two salt solutions is the same at 25° as at 18°. The validity of this assumption was affirmed by comparing the ratios of the conductances of potassium chloride solutions with those of potassium chlorate and bromate at the same two temperatures. The potential data thus obtained are collected in Table I. The solutions in all cells were under an atmosphere of pure nitrogen.

TABLE I

THE ELECTROMOTIVE FORCES OF CALOMEL–IODATE CELLS AT 25 ± 0.02°

m	0.20	0.10	0.05	0.01
E_t, volt	.0850	.0833	.0825	.0810
E_l, volt	.0096	.0087	.0082	.0075
E_{298}, volt	.0946	.0920	.0907	.0885

To calculate the potentials of the iodate electrodes in the given potassium iodate solutions it is only necessary to add the potentials of the calomel electrodes in the same concentrations of potassium chloride. The latter were calculated by means of the equation: $E = E^\circ - 0.05915 \log a_{Cl^-}$, using for the potential of the electrode, Hg, Hg_2Cl_2, $Cl^-(a = 1)$, $E^\circ = 0.2676$ volt,[5] and the activity coefficients as obtained by Harned[6] for potassium chloride. The potentials of the calomel electrodes thus calculated are given in Table II. By adding these potentials to the total potentials, E_{298}, of the calomel–iodate cells, Table I, we obtain directly the potentials of the electrode: Ag,$AgIO_3$,$KIO_3(m)$, in the various concentrations of potassium iodate. These electrode potentials are given in the fifth column of Table II.

TABLE II

THE POTENTIALS OF THE CALOMEL AND SILVER IODATE ELECTRODES AT 25°

m	γ[6] KCl	γ[3] KIO_3	E_{298} Calomel	E_{298} Iodate	E°_{298} Iodate
0.20	0.712	...	0.3178	0.4124	...
.10	.764	0.692	.3336	.4256	0.3571
.05	.815	.765	.3498	.4405	.3567
.01	.899	.882	.3886	.4771	.3552

Two methods are available for calculating E° for the silver–silver iodate electrode. The potential E° is given by the equation

$$E = E^\circ - 0.05915 \log a_{IO_3^-} \quad (1)$$

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[4] "International Critical Tables," 1929, Vol. VI, pp. 234 and 252.

[5] *Ibid.*, 1929, Vol. VI, p. 332.

[6] Harned, THIS JOURNAL, 51, 416 (1929).

Subtracting 0.05915 log $m_{IO_3^-}$ from both sides of (1), we obtain a modified form of a relation employed by Lewis and Randall[7]

$$0.05915 \log (a/m)_{IO_3^-} = E^\circ - (E + 0.05915 \log m_{IO_3^-})$$

The log a/m is equal to zero at infinite dilution and hence $E^\circ = (E + 0.05915 \log m_{IO_3^-})$. If we plot the quantity in parentheses against the square root of the molality, the intercept on the ordinate at $m = 0$ is equal to E°.

Since extrapolation is precarious in any case, and because of possible errors in determining the potential of the most dilute solution, which was the most difficult to obtain, we have calculated the potential, E°_{298}, by (1), using accepted values[8] for the activity coefficients of potassium iodate. The values of E°, which should be the same at all concentrations, are given in the last column of Table II. It is evident that the potential of the 0.01 m electrode is too low. Omitting this, we take as the most probable value of the potential of the Ag, $AgIO_3$, IO_3^-, ($a = 1$) electrode, $E^\circ_{298} = 0.3569$ volt.

Summary

The electromotive forces of a series of cells of the type: Hg,Hg_2Cl_2,KCl-(m),KIO_3,$AgIO_3$,Ag, have been measured at 25°. By combining these values with the potentials of the corresponding calomel electrodes, the potential of the Ag,$AgIO_3$,IO^- ($a = 1$) electrode is found to be, $E^\circ_{298} = 0.3569$ volt.

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(7) Lewis and Randall, "Thermodynamics," 1923, p. 334.

(8) Lewis and Randall, *ibid.*, p. 362.

IOWA CITY, IOWA

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[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Optical Properties of the Double Salt $(NH_4)_2SO_4{\cdot}CaSO_4{\cdot}2H_2O$

BY ALBERT R. MERZ, JOHN O. HARDESTY AND STERLING B. HENDRICKS

During the course of an investigation of the hygroscopicities of mixtures of fertilizer salts not having common ions,[1] one of the solid phases obtained in the systems, $NH_4^+Ca^{++}NO_3^-SO_4^=$ and $NH_4^+Ca^{++}H_2PO_4^-SO_4^=$, was found to be a double salt of calcium and ammonium sulfates. Three double salts, in which the ratios of ammonium sulfate to calcium sulfate are 1:1, 1:2 and 1:5, respectively, have been reported in the literature. The double salt with the ratio 1:2 does not exist below 75°[2] and, as the vapor pressure measurements were carried out at 30°, it therefore remained to identify the salt as one of the other two compounds. Since the double salt with the ratio, 1:5, cannot exist, in the system $NH_4^+Ca^{++}SO_4^=$, in contact with solid ammonium sulfate,[2] gypsum was added to a saturated solution of ammonium sulfate which was then evaporated until considerable ammonium sulfate had crystallized and finally allowed to stand for several days. Microscopic examination of the solid phases disclosed both ammonium sulfate and the same double salt as was found present during the vapor pressure determinations, thus indicating that the double salt in question had the 1:1 ratio.

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[1] A. R. Merz, W. H. Fry, J. O. Hardesty and J. R. Adams, *Ind. Eng. Chem.*, **25**, 136 (1933).

[2] J. D'Ans and O. Schreiner, *Z. anorg. Chem.*, **62**, 141 (1909).

D'Ans and Schreiner[2] state that the double salt of ammonium and calcium sulfate having the 1:1 ratio is an ammonium syngenite, analogous in composition to syngenite, and forms in a saturated ammonium sulfate solution according to the reaction $(NH_4)_2SO_4 + CaSO_4 \cdot 2H_2O = (NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O + H_2O$. Bell and Taber,[3] however, claim that the compound contains two molecules of water of crystallization and should be given the formula $(NH_4)_2SO_4 \cdot CaSO_4 \cdot 2H_2O$. Since the optical properties and density of this salt appear not to have been reported, it was considered desirable to determine them, especially as the information thus gained would aid in settling the question as to its composition.

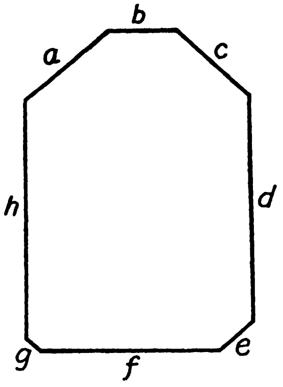

Fig. 1b.

Fig. 1a.

To obtain the double salt as the sole phase in contact with the liquid phase, 251 g. of ammonium sulfate, 36.65 g. of gypsum and 1500 cc. of water were evaporated at 30° over a period of eight days to a volume of 500 cc. to give a point in the field of the 1:1 salt.[4] Microscopic examination showed the solid phase to consist only of crystals identical with those of the double salt previously obtained. Since washing the salt with water quickly decomposes it, leaving gypsum as a residue, and washing with alcohol–water and alcohol–ether, as carried out by D'Ans,[5] has been shown by Bell and Taber to result in decomposition also, the method of residues was used for the chemical determination of the composition. The material used for the optical work was obtained separately by suction filtration and air drying.

Analysis of the mother liquors gave water 63.99%, ammonium sulfate 35.69% and calcium sulfate 0.32%; of the moist crystals, water 32.82%, ammonium sulfate 40.39% and calcium sulfate 26.79%, whence by calculation or graphically, using triangular coördinates, the dry double salt contains 11.47% water of crystallization. This corresponds to the theoretical value, 11.84%.

(3) J. M. Bell and W. C. Taber, *J. Phys. Chem.*, **11**, 492 (1907).

(4) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. IV, p. 388.

(5) J. D'ans, *Ber.*, **39**, 3326 (1906).

Optical Properties.—The common crystal habit is that shown in Fig. 1a. A centered acute bisectrix interference figure was obtained from some flat needles of this type. The direction of vibration of the slowest ray, γ, is parallel to the elongation. A very few crystals of the type shown in Fig. 1b were observed in wet samples. The angles ah, cd, and de are equal as measured under the microscope. The crystal section was apparently perpendicular to the optic normal.

The indices of refraction ascertained by the immersion method are N_D: $\alpha = 1.522$; $\beta = 1.527$; $\gamma = 1.529$. The crystals are optically negative.

The density, measured by the centrifugal suspension method, is 2.07. Greater accuracy was impossible owing to the minuteness of the dried crystals.

It is interesting to compare the optical properties of this compound with those of ammonium sulfate and gypsum.[6]

	$(NH_4)_2SO_4$ mascagnite	$CaSO_4·2H_2O$ gypsum		$(NH_4)_2SO_4·CaSO_4·2H_2O$
α	1.521	1.5195	1.5208	1.522
β	1.523	1.5216	1.5230	1.527
γ	1.533	1.5283	1.5305	1.529
d_{20}	1.7681[7]	2.32[8]		2.07
Crystal system	Orthorhombic	Monoclinic		Orthorhombic?
Mol. vol.	74.74 cc.	74.2 cc.		147 cc.
Mol. refractivity (calcd. by Lorenz–Lorentz formula)	22.89	22.67	22.85	45.12

The value of the molecular refractivity of $(NH_4)_2SO_4·CaSO_4·2H_2O$ is, within the limit of error, equal to the sum of the values for $CaSO_4·2H_2O$ and $(NH_4)_2SO_4$. This is likewise true for the molecular volumes. These facts further confirm the composition of the hydrated double salt as being $(NH_4)_2SO_4·CaSO_4·2H_2O$.

WASHINGTON, D. C.

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(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1930, Vol. VII, pp. 19, 24.

(7) *Ibid.*, 1928, Vol. III, p. 44.

(8) *Ibid.*, 1926, Vol. I, p. 143.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

The Character of the Absorption of Some Amines in the Near Infra-red[1]

BY URNER LIDDEL AND OLIVER R. WULF

Observations in the infra-red on the spectra associated with the CH, NH, OH and SH groups in aliphatic and aromatic organic molecules[2] have shown that such investigations constitute a fruitful approach to a study of differentiating characteristics of these molecules. At the suggestion of Dr. F. G. Cottrell, the authors have undertaken an investigation of a considerable number of aromatic and aliphatic amines for the purpose of correlating characteristic differences in their spectra, in so far as possible, with the known chemical properties of these molecules.[3] In view of the importance attached by organic chemists to the electrical characteristics of portions of molecules in connection with their chemical properties, we were early convinced that the usefulness of such a study would be greatly increased by a quantitative determination of some physical property characteristic of the radical or group being studied and it was decided to measure the absorption coefficient in the region of characteristic N–H absorption.[4] A beginning has now been made on this, and we are communicating in this paper the first results of a study of a number of amines in carbon tetrachloride solution working with the absorption lying in the vicinity of 1.50μ which is due to the N–H portion of the molecule.[5]

Experimental

The infra-red glass spectrograph used throughout this present work has been described by Brackett and Liddel.[6] The excellent operating characteristics of this instrument have contributed greatly to the present work. Illustrative records for solutions of aniline and phenol in carbon tetrachloride under the conditions of slit width used in the present work are shown in Fig. 1, these being records of galvanometer deflections with wave length, and except in the positions of characteristic absorption of the compounds and the water vapor in the light path, they are records in arbitrary units, of the radiation from the tungsten lamp source modified by the transmission of the optical parts of the instrument. Certain characteristic absorptions are indicated. Determination of the absorption coefficients was carried out by recording at appropriate intervals on the experimental plate segments of both the base line of no galvanometer deflection (shutter introduced corresponding to complete opacity), and of the intensity of the lamp source by way of a second optical system carrying the light to the slit around the absorption cell rather than through it. Before and after each experimental plate a complete record was taken under the same conditions except that the cell contained pure carbon tetrachloride instead of the solution of the amine being studied. From the average of these two records it was possible to determine the curve of the galvanometer trace on the solution plate as it would have been had not the solute been present in the solution and to the same scale as this solution plate, even in the event of appreciable zero drift in the galvanometer reading and of changes in the lamp intensity with time, by using these traces of the base line and of the lamp intensity by way of the constant auxiliary light path, which are contained on all records. Thus one has a measure of the intensity of the radiation after passing through the solution and after passing through the same cell containing carbon tetrachloride but without the solute, hence the transmission of the solute. Since the concentration of the solution is known, the transmission for a definite number of molecules in the light path is known, and hence the absorption coefficient over the region of the spectrum covered may be calculated.

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[1] This paper was presented before the Organic Division of the American Chemical Society at Washington, March 28, 1933.

[2] See for example Schaefer and Matossi, "Das ultra-rot Spectrum," Julius Springer, Berlin, 1930.

[3] Lack of a particular sort of chemical evidence plus the lack of adequate interpretation of the absorption differences as yet constitute a barrier to a definite correlation in the present paper.

[4] For previous work on the study of absorption coefficients in regions of absorption due to H linked with other elements, see Bonino, *Trans. Faraday Soc.*, **25**, 876 (1929), and reference (2).

[5] Ellis, THIS JOURNAL, **49**, 347 (1927); **50**, 685 (1928).

[6] Brackett and Liddel, *Smithsonian Misc. Coll.*, **85**, No. 5 (1931).

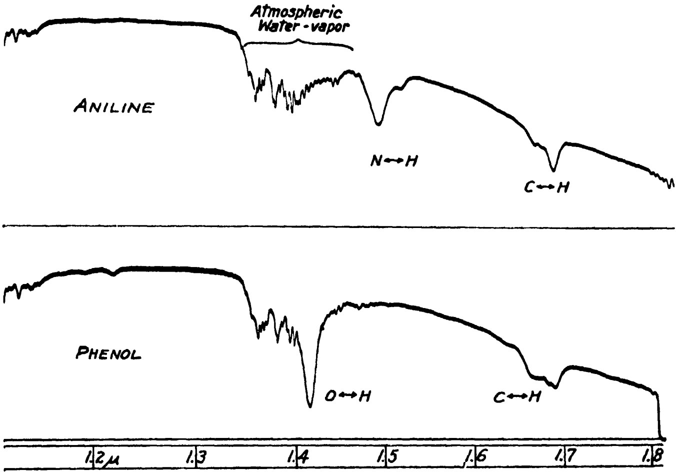


Fig. 1.—Illustrative records of aniline and phenol with characteristic absorptions indicated.

A small correction to the observed deflections was necessary owing to the presence of a certain amount of scattered light in the spectrograph. The determination of this correction was accomplished in the following manner. A measurement was made of the transmission of a certain concentration of aniline which reduced the intensity at the peak of the N–H absorption to roughly 70%. This value, which is a little in error owing to stray light, was used to compute a path length at the same concentration which would reduce the intensity at this same wave length to a fraction of 1% and the apparent intensity was then noted using this absorption. It showed a value of nearly 5%. This difference was taken as the fraction of the total deflection at this wave length that was due to scattered light, after applying a small additional correction. In the observation using the highly absorbing path of aniline, the stray light itself was somewhat reduced owing to the reduction of the total radiation entering the spectrograph. This latter was estimated as roughly 7% from the records themselves. In the case of the weakly absorbing paths ordinarily worked with, then, the stray light would be greater than the above by roughly 7% of itself. Therefore 5% of the deflection at this wave length in the absence of the solute or in the presence of weak N–H absorption seems a satisfactory estimate of stray light. To illustrate that this correction is small, the results for aniline solution containing 10^{20} molecules per square centimeter cross section of the light path may be cited. At the peak of absorption, the observed ratio of I/I_0 was found to be

0.67. If now both of the intensities making up the ratio are high by about 5%, the corrected ratio becomes 0.64. Thus, at the present stage of this research, while the correction is of sufficient importance to be taken into account, a small error in the estimation of the correction is not serious.

The estimate of stray light was also carried out in a constant path length at two different concentrations, reducing in this way the intensity in the same ratio as was mentioned above in the case where constant concentration and two different path lengths were used. The procedure at two different concentrations involves Beer's law, and a test of this law was made with aniline over a concentration range from 0.033 to 0.41 molal. Beer's law was followed within the limits of error of our measurements. At these dilutions this is not surprising, though in very concentrated solutions this law would undoubtedly fail.[4]

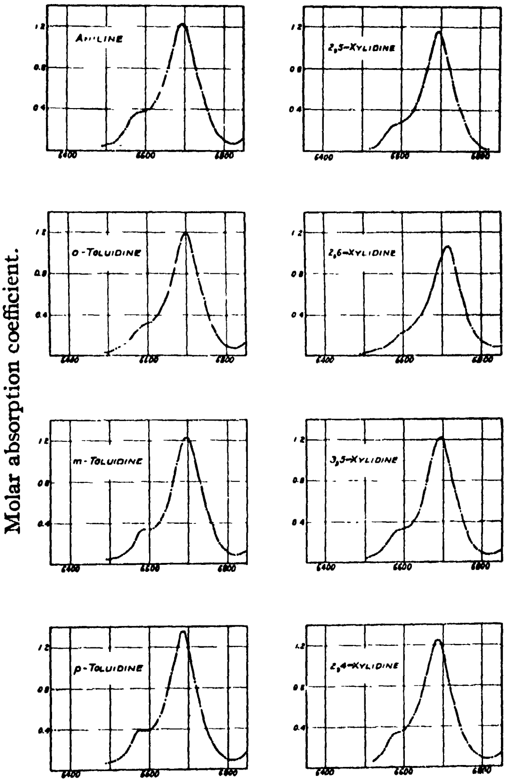
We have worked chiefly in a cell length of 5 cm. and a concentration of solute such that 10^{20} molecules are contained in one sq. cm. of light path, thus a concentration of 0.033 molal. Variations from this are noted in the table of results. All the amines have been studied in carbon tetrachloride solution. Many were originally Eastman Kodak Co. products, and, where we had reason to expect impurities, from age, discoloration, etc., redistillation or recrystallization was performed. β,β,β-Triphenylethylamine and γ,γ,γ-triphenylpropylamine were very kindly supplied by Professor L. Hellerman of the Johns Hopkins University, having been prepared by Dr. R. L. Garner. β-Phenylethylamine and γ-phenylpropylamine were supplied through the courtesy of Dr. W. H. Carothers of the du Pont Co. From a study of the boiling and melting points of the products finally used we believe that in no case, unless mentioned explicitly below, were impurities present to an extent of more than a few per cent. and usually much less. Since experience would not lead one to expect the presence of any substance having a much greater absorption power than the amine being studied and at the same position in wave length, we feel that the purity of the compounds has been ample to justify the conclusions which have been arrived at in this preliminary study. The principal conclusions are based upon the consistency of the data rather than the results of any one substance. The presence of any impurity not an amine, in any given percentage, could only affect the results by making our calculations of absorption coefficients too low by that amount.

Regarding the improbability of the presence of any highly absorbing impurity in this same region it should be pointed out that this region is apt to be rather free from possible trouble. Strong absorption depending upon electronic transitions rarely if ever comes so deep in the infra-red, so far as is known, while the absorption due to the oscillation of heavy masses, such as C–C, lie far enough in the infra-red that even their first overtones (higher overtones would be of such low intensity as to render them unimportant) are well beyond 1.5μ. Only the absorption associated in part at least with the oscillation in a H linkage can very well enter here. For these reasons, the question of small amounts of impurities in the materials studied is probably not a serious one in any case. Furthermore, fortunately, moderate absorption occurs in the first overtones of many H linkages in moderate path lengths of dilute solutions, thus, as in the present work, some hundredths molal in paths of a few centimeters. Solvents whose molecules possess only heavy atoms, such as carbon tetrachloride or tetrachloroethylene, are of course free of absorption in this region unless impurities, such as chloroform in carbon tetrachloride, are present. This region of wave length seems thus rather well adapted to the purpose of the present paper.

Results

The absorption curves to follow are plots of the absorption coefficient ϵ against frequency of absorption in cm.$^{-1}$; $\epsilon = \log_{10} I/I_0/cd$, the units being those commonly employed, c in moles per liter and d in centimeters. We do not feel justified in claiming a greater absolute accuracy than ±0.05 in the values of ϵ and ±8 cm.$^{-1}$ in frequency. Some differences in the curves within these limits are probably real, since the magnitude of some effects is undoubtedly small, even beyond detection in the present experiments.

The points on the curves represent the calculated values for the absorption coefficient determined from the records themselves and the lines are interpolations of these points. Measurements for calculation of absorption coefficients were made from the records at arbitrary wave lengths, hence points were not always read at the exact peaks of absorption; however, close visual comparisons of the original records with the drawn curves of absorption, given in the results to follow, showed their exact similarity.

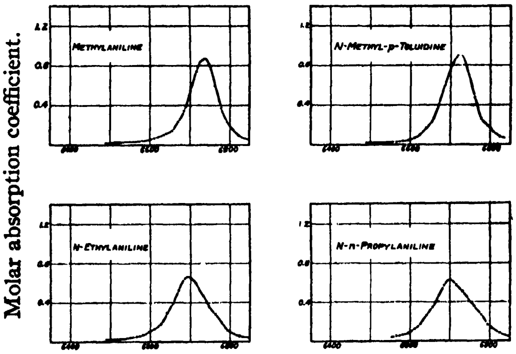


Frequency of absorption in cm.$^{-1}$.

Fig. 2.

A series of aromatic amines was chosen to observe the effects, if any, of the substitution of a methyl group for one or two of the hydrogen atoms in various positions of the aromatic nucleus on the absorption of the NH portion. All the primary amines (Fig. 2) are very similar, both in the form of the curve and intensity of absorption. However, small differences occur, reproduced on two independent sets of data of which the average is recorded. Aniline has a fairly symmetrical absorption with a maximum at 6693 cm.$^{-1}$, and another much weaker band around 6600 cm.$^{-1}$ unresolved from the main peak. Methyl substitution ortho to the amine group reduces the absorption in the region of 6600 cm.$^{-1}$ and apparently shifts the median of the main absorption to very slightly higher frequency. Substitution in the meta position has no obvious effect, and in the para position shifts the peak to lower frequencies and increases the absorption coefficient of the peak. In the xylidines, substitution of the second methyl group seems to have only the added effect of the methyl group in the second position; *i. e.*, 3,5-xylidine is exactly like *m*-toluidine; 2,4-xylidine a rough composite of ortho and para toluidines. It must be mentioned that there is real absorption in the vicinity of 6950 cm.$^{-1}$ which apparently varies in intensity with the long wave length dissymmetry of the bands, *i. e.*, in *p*-toluidine and aniline, it is appreciable, and in 2,6-xylidine it is negligible; however, its apparent variation with the dissymmetry of the peak would suggest a definite relation which should be investigated. No measurements can be given on this absorption at the present time, since it lies in the midst of strong absorption, due to water vapor, which, although removable with this spectrograph, we are using as a check on the dispersion of the instrument.

A methyl group attached to the N atom of aniline and *p*-toluidine decreases the intensity of absorption to about two-thirds that of the corresponding primary amine and very appreciably increases the frequency of absorption of the remaining N–H bond, whereas an ethyl group in aniline decreases the absorption to one-half and has no effect on the main frequency. In propylaniline the intensity is the same as ethylaniline, though absorption occurs at a slightly higher frequency. Thus the absorption per N–H bond is about the same in ethyl- and propylaniline as in aniline, but greater in methylaniline by some 35%. In all these compounds the absorptions at 6600 cm.$^{-1}$ and around 6950 cm.$^{-1}$ have so diminished as to be no longer observable (Fig. 3).

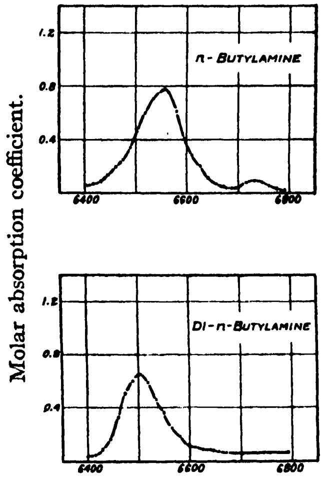


Frequency of absorption in cm.$^{-1}$.

Fig. 3.

The normal aliphatic primary amines are characterized by an appreciable decrease in the absorption coefficient compared with the aromatic amines, as well as the known[6] shift in the frequency of absorption. A very interesting result is the exact similarity within experimental error of the curves for *n*-propyl, butyl, amyl and heptyl amines, so that only the curve for *n*-butylamine is given in Fig. 4. The same is true for the secondary amines di-*n*-propyl, di-*n*-butyl and di-*n*-amyl. These differ from the primary amines in having a lower absorption coefficient, which, however, is greater per N–H bond by about 50% in the secondary than in the primary amines. The peak of absorption is at a longer wave length, 6504 cm.$^{-1}$ compared to 6556 cm.$^{-1}$ for the primary.

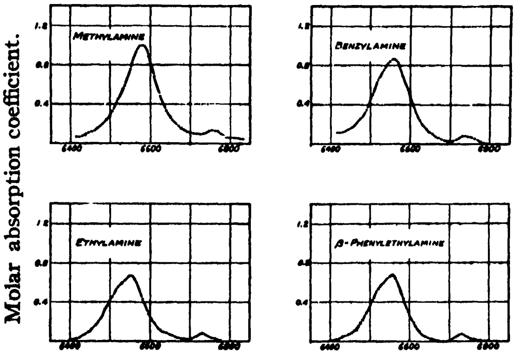
Methylamine (Fig. 5) differs from the foregoing aliphatic amines by absorbing at a higher frequency and with greater intensity, while ethylamine differs oppositely. Benzylamine, β-phenylethylamine and γ-phenylpropylamine are to all appearances normal aliphatic amines, as to shape of the curve and frequency of absorption, except that benzylamine absorbs with slightly greater intensity and β-phenylethylamine possibly slightly less. The intensity measurements of these latter two, however, are not reliable, and no measurements at all can be given for the phenylpropylamine, due to a peculiar reaction between these compounds and the solvent, carbon tetrachloride, increasing in speed with the length of the carbon chain, so that in γ-phenylpropylamine a record suitable only for wave length determinations could be obtained. It was observed that reaction occurred between the solvent and many other of the amines after several days, causing, however, no experimental difficulties over the short time required for experimental work. These reactions will be the subject of a note soon to be published by Dr. L. B. Howard.



Frequency of absorption in cm.$^{-1}$

Fig. 4.

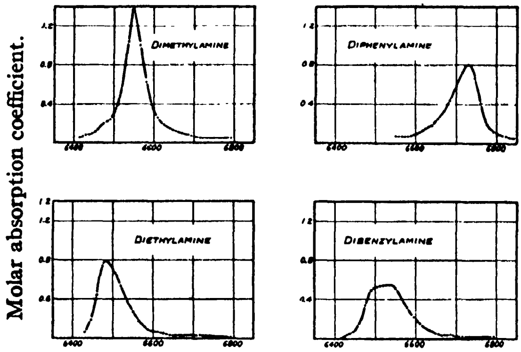
The secondary amines shown in Fig. 6 differ markedly among themselves and from their corresponding primary compounds. The only secondary aromatic amine we have been able to obtain is diphenylamine, which absorbs at a higher frequency than aniline, has only one apparent absorption maximum, but here again with an intensity value greater than one-half that of aniline, and by about 35%. Dimethylamine has a quite symmetrically peaked absorption but an intensity greater than one-half methylamine by about 180%. The absorption of diethylamine has only one apparent maximum, which is greater in intensity than ethylamine. The absorption curve of dibenzylamine is perhaps the oddest of all, and leads to suspicion of impurities; however, careful redistillation of the amine *in vacuo* failed to have any effect on the absorption, and also the carbylamine reaction for the presence of primary amines was entirely negative.



Frequency of absorption in cm.$^{-1}$.

Fig. 5.

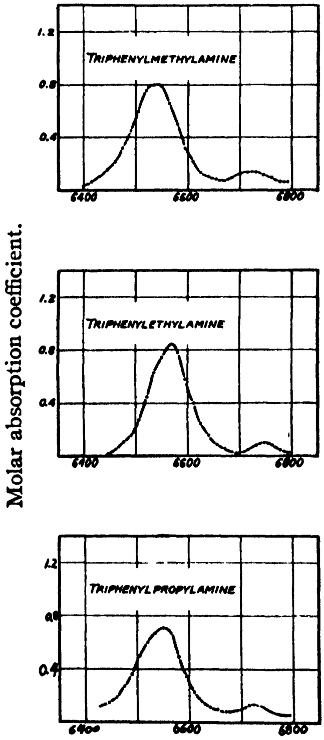
Triphenylpropylamine (Fig. 7) is very similar in shape and position to benzylamine; the median of the absorption of triphenylmethylamine lies at a slightly longer wave length, of triphenylethylamine at slightly shorter wave length. Although these compounds were probably quite pure no certain measurement of the purity could be obtained, hence no emphasis can be placed on the alternation in intensity of absorption at the maximum in this series.



Frequency of absorption in cm.$^{-1}$.
Fig. 6.

As examples of other types of amines, the absorption of pyrrole and fluorylamine is shown (Fig. 8). Fluorylamine has a distinctly aliphatic type of absorption, very similar to benzylamine, absorbing with possibly slightly greater intensity, and at somewhat longer wave lengths. The absorption of pyrrole apparently consists of a single intense band, greater in intensity at the peak than any other amine studied, and lying at the highest frequency observed, which might not be unexpected, on account of the linking of the N atom to two ethylenic carbon atoms.

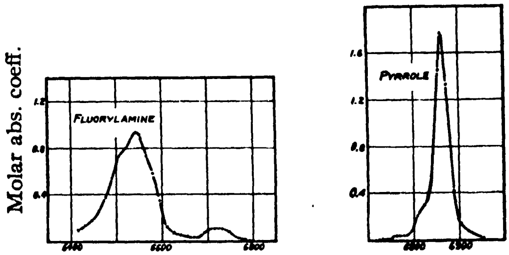
Since a composite of the curves of diphenylamine and *n*-propylamine in certain concentrations might result in a curve similar to that of *p*-toluidine, records of a mixed solution of these in concentrations purposely chosen to resemble as nearly as possible *p*-toluidine were clearly differentiable from the latter by the separation of the maxima, there being no close resemblance.



Frequency of absorption in cm.$^{-1}$.
Fig. 7.

Discussion

While the present results are preliminary in a study to be continued and extended to a much greater number of types of amines, they seem to indicate a few important facts. First, the absorption coefficient for the N–H bond in its absorption at 1.5μ throughout a very considerable range in character of the compounds, comprising aliphatic and aromatic primary and secondary amines, remains of the same order of magnitude. Second, there are measurable differences in this absorption coefficient from class to class, *i. e.*, primary aliphatic, secondary aliphatic, primary aromatic, and secondary aromatic, as well as differences in the position of the maximum of the absorption. Third, when a normal paraffin radical greater than two carbon atoms long is attached to the amine group, the absorption coefficient and position of the maximum of absorption vary very little, less than our present ability to detect. A similar remark holds for the corresponding secondary aliphatic amines, the absorption per N–H bond being somewhat greater in this group than in the former. A measurable variation is found within the primary aromatic amines studied, a dissymmetry in the absorption appearing in varying amounts in these compounds and perhaps accounting for the variation in the total absorption and in the position of the maximum within this group. Only one secondary purely aromatic amine has been studied, diphenylamine. It has a greater absorption coefficient per N–H bond and a different position of the maximum than has aniline, its closest analog in the primary group, thus exhibiting a behavior somewhat similar to that observed in the aliphatic amines. However, it should be pointed out that in the case of the aliphatic amines the secondary amine maximum was shifted to lower frequency, while in the aromatic amines diphenylamine had its maximum at a higher frequency than aniline.



Frequency of absorption in cm.$^{-1}$.

Fig. 8.

The first point mentioned above suggests the use of this quantitative data as a method of determining the total number of N–H bonds present in a given amount of unknown substance. Thus, for example, it is possible that it may be applied in this way to a study of such molecules as the alkaloids and chlorophyll. The second point suggests that a differentiation between classes may be possible from the differentiation in the position of the maximum of absorption, the quantitative measure of the absorption coefficient of the N–H bond for the respective classes making possible a determination of the number of N–H bonds of any one kind present by a method which seemingly may be brought to considerable accuracy. The third point, interesting but less useful, may permit a certain amount of differentiation within the primary aromatic amines. It is proposed to utilize the first two points in the extension of this work and to continue the work to the other commonly occurring forms of the N–H group as well, for example pyrroles, imines, etc. Also, it should be possible to carry these measurements to other solvents, in some cases more suitable than carbon tetrachloride, such as tetrachlorethylene, and in a similar way to the above, to the O–H and S–H bonds. In principle also it could be carried to the C–H bond, though in organic molecules the practical application of the latter might be limited to compounds containing only a few C–H groups. Spectra are now being recorded in this Laboratory of some aliphatic and aromatic hydrocarbons enabling a study of this last point.

VALUES OF THE ABSORPTIONS AT THEIR MAXIMA

	ν, cm.$^{-1}$	λ (μ)	ϵ	ϵ/N–H bond	Remarks
Ammonia	6571	1.522	0.54	0.18	0.0458 *M* soln.
Methylamine	6576	1.521	1.00	.50	0.066 *M* soln.
Ethylamine	6549	1.527	0.67	.34	0.1086 *M* soln.
n-Propylamine	6556	1.525	.78	.39	I_0[a] reduced 3%
n-Butylamine	6556	1.525	.78	.39	
n-Amylamine	6556	1.525	.78	.39	
n-Heptylamine	6556	1.525	.82	.41	
Dimethylamine	6546	1.528	1.40	1.40	0.0288 *M* soln.
Diethylamine	6482	1.543	0.77	0.77	
Di-*n*-propylamine	6504	1.537	.61	.61	
Di-*n*-propylamine	6504	1.537	.64	.64	
Di-*n*-amylamine	6504	1.537	.60	.60	
Aniline	6693	1.494	1.22	.61	
o-Toluidine	6703	1.492	1.19	.60	
m-Toluidine	6693	1.494	1.22	.61	
p-Toluidine	6685	1.496	1.35	.68	
2,5-Xylidine	6699	1.493	1.16	.58	
2,6-Xylidine	6716	1.489	1.06	.53	
3,5-Xylidine	6693	1.494	1.22	.61	
2,4-Xylidine	6685	1.496	1.24	.62	
Methylaniline	6730	1.486	0.86	.86	
Ethylaniline	6693	1.494	.64	.64	
Propylaniline	6700	1.492	.63	.63	
N-Methyl-*p*-toluidine	6725	1.487	.89	.89	
Diphenylamine	6730	1.486	.80	.80	
Dibenzylamine	6500–6530	1.53–1.54	.55	.55	
Benzylamine	6556	1.525	.86	.43	I_0[a] reduced 7%
β-Phenylethylamine	6556	1.525	.68	.34	0.0446 *M* soln.
γ-Phenylpropylamine	6556	1.525	...	...	I_0[a] reduced 8%
Triphenylmethylamine	6534	1.530	.80	.40	
Triphenylethylamine	6564	1.523	.83	.42	I_0[a] reduced 16%
Triphenylpropylamine	6549	1.527	.71	.36	
Fluorylamine	6541	1.529	.93	.47	
Pyrrole	6859	1.458	1.77	1.77	

[a] In calculation of the transmission coefficients of this solution, which was slightly turbid, this value was used as the correction factor, and was determined on the basis of 100% transmission at 6300 cm.$^{-1}$.

The authors gratefully acknowledge the interest of Dr. F. G. Cottrell, and the assistance of Drs. G. E. Hilbert and L. B. Howard, as well as valuable discussions with other members of the Staff of the Fixed Nitrogen Research Laboratory.

Summary

Absorption coefficients have been measured in the absorption lying at about 1.5μ due to the N–H group in a number of primary and secondary aliphatic and aromatic amines, and the positions of the maxima of absorption have been determined.

A method is suggested for the utilization of such data, as yet in a somewhat restricted field, for the detection of the presence of N–H groups, and for the approximate determination of the number of N–H groups present per cubic centimeter of a solution as well as the way in which this group is linked in the molecule.

WASHINGTON, D. C.

RECEIVED APRIL 28, 1933
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Complex Compounds in Eder's Solution

BY G. H. CARTLEDGE AND S. L. GOLDHEIM[1]

Several attempts have been made to explain the mechanism of Eder's reaction, $2HgCl_2 + C_2O_4^{=} \longrightarrow Hg_2Cl_2 + 2CO_2 + 2Cl^-$. Most of the students of this reaction have assumed, as will be pointed out later in the discussion of their work, that the photochemical properties of this solution of oxalate and mercuric chloride are dependent on a mercuri-oxalate complex.

The present work was undertaken in order to determine the nature of the complexes which exist in Eder's solution and the extent to which they form. This information was sought by: (1) experiments on the partition of mercuric chloride between benzene and aqueous oxalate solutions, and (2) determinations of the freezing point depressions in Eder mixtures. Preliminary freezing point experiments made in this Laboratory by Mr. F. B. Slagle showed that the formation of the complex or complexes is attended by a small diminution in the number of molecules.

Since chloride ion is known to have a marked effect on the reaction and is also known to form complexes with mercuric chloride, a careful study of the literature on mercuri-chloro complexes as well as that on mercuri-oxalate complexes was made.

Throughout this work, the ionization of mercuric chloride is neglected, the figures given by Drucker,[2] $(Hg^{++})(Cl^-)^2/(HgCl_2) = 0.95 \cdot 10^{-14}$ at 25° and $(Hg^{++})(Cl^-)/(HgCl^+) = 5.3 \cdot 10^{-8}$ at 25°, showing that this assumption is permissible.

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[1] This paper is abstracted from the dissertation presented by S. L. Goldheim to the Faculty of Philosophy of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Literature

Mercuri-oxalate Complexes.—Roloff[3] attempted to show by the rather dubious ebullioscopic method the presence of complexes such as $(NH_4)_2Hg(C_2O_4)Cl_2$, $(NH_4)_2Hg_2(C_2O_4)_2Cl_2$ and others. Berger[4] assumed the presence of a complex without giving its formula. Bekhterev[5] has also mentioned the presence of complex mercury salts in Eder's solution. Other workers have studied the system $K_2C_2O_4$–HgC_2O_4–H_2O and found definite complexes, which are, of course, solid salts in equilibrium with saturated solutions.

Mercuri-chloro Complexes.—A great mass of conflicting data on these complexes exists. A critical study of forty-four articles on this subject leads to the conclusion that the work of Linhart[6] is the most definite and quantitatively accurate. This work shows that in solutions of mercuric chloride and alkali chloride (represented by MCl) below 40° the following molecular species may exist: $HgCl_2$, Hg_2Cl_4, MCl, M^+, Cl^-, $MHgCl_3$, $HgCl_3^-$, M_2HgCl_4, $HgCl_4^=$, MHg_2Cl_5, $Hg_2Cl_5^-$, $M_2Hg_2Cl_6$, $Hg_2Cl_6^=$. We neglect any ionization of $HgCl_2$ or Hg_2Cl_4. The proportions of these species in any solution depend chiefly on the concentrations. With the mercuric chloride in excess of the alkali chloride, the complexes are those having the greater proportion of mercury. The equilibrium constants necessary for calculations of these species are known from Linhart's work, which is used as the basis for the present research.

Theoretical

A scheme of complex formation in Eder's solution which would satisfy three points has been sought: first, the distribution experiments; second, the measurements of freezing point depressions; and, third, the known reaction rates, assuming that the reaction is, as has been suggested, a decomposition of the mercuri-oxalate complex.

The following schemes were tried

$$HgCl_2 + 2C_2O_4^= \rightleftarrows Hg(C_2O_4)_2^= + 2Cl^- \qquad (1)$$
$$Hg_2Cl_4 + 4C_2O_4^= \rightleftarrows Hg_2(C_2O_4)_4^{----} + 4Cl^- \qquad (2)$$
$$HgCl_2 + C_2O_4^= \rightleftarrows HgClC_2O_4^- + Cl^- \qquad (3)$$
$$HgCl_2 + C_2O_4^= \rightleftarrows HgCl_2C_2O_4^= \qquad (4)$$
$$Hg_2Cl_4 + C_2O_4^= \rightleftarrows Hg_2Cl_4C_2O_4^= \qquad (5a)$$
$$2HgCl_2 + C_2O_4^= \rightleftarrows Hg_2Cl_4C_2O_4^= \qquad (5b)$$
$$Hg_2Cl_4 + C_2O_4^= \rightleftarrows Hg_2Cl_2C_2O_4 + 2Cl^- \qquad (6a)$$
$$2HgCl_2 + C_2O_4^= \rightleftarrows Hg_2Cl_2C_2O_4 + 2Cl^- \qquad (6b)$$

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(2) Drucker, *Z. Elektrochem.*, **18**, 236 (1912).

(3) Roloff, *Z. physik. Chem.*, **13**, 327 (1894).

(4) Berger, *Rec. trav. chim.*, **40**, 387 (1921).

(5) Bekhterev, *J. Russ. Phys.-Chem. Soc.*, **57**, 161 (1925); *Chem. Abstr.*, **20**, 2459 (1926).

(6) Linhart, THIS JOURNAL, **37**, 258 (1915); **38**, 1272 (1916).

$$2HgCl_2 + 2C_2O_4^{=} \rightleftarrows Hg_2Cl(C_2O_4)_2^{-} + 3Cl^{-} \quad (7)$$
$$Hg_2Cl_4 + 2C_2O_4^{=} \rightleftarrows Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^{-} \quad (8a)$$
$$2HgCl_2 + 2C_2O_4^{=} \rightleftarrows Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^{-} \quad (8b)$$

The distribution measurements lead to equilibrium constants for schemes 1 to 7 showing decided drifts in these values when arranged in the order of varying ratio of bichloride to oxalate. The constant is the same for (8a) and (8b) and shows no drift. Measurements of the freezing point depressions, however, show that (8b) is the correct representation, and an additional reason for adopting this scheme is that this permits an explanation of certain of the reported reaction rate measurements.

In the distribution experiments successive portions of Eder's solution were shaken with benzene until the mercuric chloride in the benzene was in equilibrium with that in the *original* aqueous solution. The concentration in the benzene was determined. Then, knowing the original concentrations of mercuric chloride and potassium oxalate, the following calculations were made. All concentrations are expressed in moles per liter.

As has been stated, the only scheme of complex formation which fits the experimental results is

$$2HgCl_2 + 2C_2O_4^{=} \rightleftarrows Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^{-} \quad (1)$$

We have at the same time the equilibria

$$2HgCl_2 \rightleftarrows Hg_2Cl_4 \quad (2)$$
$$HgCl_2 + Cl^{-} \rightleftarrows HgCl_3^{-} \quad (3)$$
$$Hg_2Cl_4 + Cl^{-} \rightleftarrows Hg_2Cl_5^{-} \quad (4)$$
$$HgCl_3^{-} + Cl^{-} \rightleftarrows HgCl_4^{=} \quad (5)$$
$$Hg_2Cl_5^{-} + Cl^{-} \rightleftarrows Hg_2Cl_6^{=} \quad (6)$$
$$Hg_2Cl_6^{-} + Cl^{-} \rightleftarrows HgCl_3^{-} + HgCl_4^{=} \quad (7)$$

Equation 7 is included for completeness but does not enter the calculations. Equation 2 fixes a relationship between $HgCl_2$ and Hg_2Cl_4. The remaining five equations contain five unknowns and yield, on inspection, five algebraic equations, containing these. The solution has been carried out, and calculations made on this basis check the results here presented. Because, however, of the large amount of arithmetic involved it has been found more satisfactory to neglect equations 5 and 6 when dealing with solutions of low chloride ion concentration, as is the case in Eder mixtures. Equations 1 to 4 then lead to the following three algebraic equations

$$\Sigma HgCl_2 = a + 2b + 2x + y + 2z$$
$$(y)/(a)(2x - y - z) = A$$
$$(z)/(b)(2x - y - z) = B$$

The symbols used in this discussion are: $(HgCl_2)_b$, the concentration in the benzene—experimentally determined; $a = (HgCl_2)_w$, the concentration in the water layer[6]—$a = 11.90(HgCl_2)_b$; $b = (Hg_2Cl_4)$, the concentration of the double molecules[6]—$b = 0.297 \cdot a^2$; $x = (Hg_2Cl_2(C_2O_4)_2^{=})$, the concentration of the oxalate complex; $y = (HgCl_3^-)$; $z = (Hg_2Cl_5^-)$; $\Sigma HgCl_2$, the original formality of mercuric chloride; $\Sigma K_2C_2O_4$, the original formality of potassium oxalate.

At equilibrium the concentration of the chloride ions will then be $(2x - y - z)$, and that of the oxalate ions will be $(\Sigma K_2C_2O_4 - 2x)$.

A and B are constants having the values 9.8 and 37, respectively.[6]

Solving the three algebraic equations (most simply by determinants), we obtain the results

$$x = (\Sigma HgCl_2 - a - 2b)(aA + bB + 1)/(2)(2aA + 3bB + 1)$$
$$y = (\Sigma HgCl_2 - a - 2b)(aA)/(2aA + 3bB + 1)$$
$$z = (\Sigma HgCl_2 - a - 2b)(bB)/(2aA + 3bB + 1)$$

Using the values of x, y and z thus obtained, the equilibrium constant of formation of the oxalate complex may be calculated

$$K' = (Hg_2Cl_2(C_2O_4)_2^=)(Cl^-)^2/(HgCl_2)^2(C_2O_4^=)^2$$
$$= (x)(2x - y - z)^2/(a)^2(\Sigma K_2C_2O_4 - 2x)^2$$

This constant, K', differs from the true equilibrium constant, K, by a factor due to the activity coefficients of the ions. If the activity coefficient is represented by γ, we will call $\gamma_{Cl^-} = \gamma_I$. To a reasonable approximation, $\gamma_{Hg_2Cl_2(C_2O_4)^=} = \gamma_{C_2O_4^=} = \gamma_{SO_4^=} = \gamma_{II}$. We may calculate the ionic strengths[7] of each solution used, and find corresponding values for γ_{Cl^-} and $\gamma_{SO_4^=}$. The constant, K, will then equal $(K')(\gamma_I)^2/(\gamma_{II})$.

In the freezing point experiments, the sum of the freezing point depressions of the separate mercuric chloride and potassium oxalate solutions is compared with the depression of the mixture containing the same concentrations of salts. For every mole of $Hg_2Cl_2(C_2O_4)_2^=$, of $HgCl_3^-$, or of $Hg_2Cl_5^-$ that is formed, the sum of all the moles in solution is reduced by one, while the effect on the equilibrium $2HgCl_2 \rightleftarrows Hg_2Cl_4$ is inappreciable (less than 0.001 mole at all the concentrations studied). Hence the product, $(1.86)(x + y + z) = \delta_{calcd.}$, should give the amount by which the depression calculated on the basis of no complex formation (that is, the sum of the depressions of the separate solutions), exceeds the actual depression. This calculated value of δ may then be compared with the observed value.

Experimental

Materials. Mercuric Chloride.—Baker C. P. salt, labeled as containing 0.001% Fe, was three times recrystallized from water and dried in an oven.

Potassium Oxalate.—Djang[8] has showed that ammonia is present in the precipitate of mercurous chloride when ammonium oxalate is used in Eder's reaction; hence potassium oxalate was used throughout this work. Baker C. P. salt, labeled as containing 0.0006% Fe, was three times recrystallized from water and dried over calcium chloride in a desiccator.

Potassium Iodate.—Kahlbaum best salt was powdered and dried in an oven.

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(7) Lewis and Randall, "Thermodynamics," 1923.

(8) Djang, Dissertation, Johns Hopkins University, 1930.

Benzene.—Baker "Thiophene-free" C. P. benzene was redistilled once in a simple distilling apparatus and the liquid boiling at 80–81° (uncorrected) was used.

Solutions.—Mercuric chloride solution was made up to the approximate concentration desired and standardized against potassium iodate according to the method of Jamieson.[9]

Potassium oxalate solution was made up approximately and standardized against potassium permanganate in the usual manner.

Potassium iodate solution was made up accurately according to Jamieson's directions.

Apparatus and Methods.—The distribution experiments were carried out in a water thermostat, painted black, kept out of direct sunlight, and regulated to 25.00 ± 0.02°. It was found convenient to shake the solutions in foil-covered hydrogenation bottles of about 250-cc. capacity. The thick walls of these diminish the possibilities of sudden temperature changes. The bottles were fitted with spring-clamped porcelain plugs, as caps, firmly seated in the necks of the bottles by means of chamois-skin washers. Such an arrangement allowed fast work with little loss of benzene by evaporation. Both aqueous and benzene layers were removed by *blowing* out in a pipet.

Two series of freezing point experiments were made, one set carried out in a one-pint Dewar flask, according to the method suggested by Richards;[10] and the other set done by the Beckmann method as usually described.[11]

Potassium oxalate concentrations were determined in the usual manner with potassium permanganate, duplicate titrations being run in practically all cases.

The analyses for mercuric chloride were in most cases made by the potassium iodate method of Jamieson, which was found by check experiments to be very satisfactory. In the freezing point experiments with pure mercuric chloride the analyses were made by measuring the density of a 10-cc. portion and reading off the molality from a curve prepared from figures collected by Comey.[12] Two of these analyses were checked by the sulfide method. In a few other cases the sulfide method was used.

The mode of procedure in the distribution experiments was as follows: 100 cc. of benzene and 50 cc. of the Eder mixture, of known concentration in mercuric chloride and potassium oxalate, were put in the bottles in the thermostat and shaken for two hours. After standing for another half to three-quarters hour, the bottom (aqueous) layer was blown out in a pipet, and a fresh 20-cc. portion of the Eder mixture added. This process was repeated until the benzene had been shaken with four portions of solution, preliminary experiments having shown that four successive shakings were needed to ensure equilibrium conditions. Shaking was found more satisfactory than stirring, equilibrium being reached in equal times. After the last shaking, the solutions again stood half to three-quarters of an hour in order to settle, and a 25-cc. sample of the benzene layer was carefully blown out from as near the top as possible. This sample was evaporated over a lamp bulb in a stream of air, fifteen to twenty minutes being required and check experiments showing that there was no detectable loss of mercuric chloride. A test with potassium permanganate showed that no detectable amount of potassium oxalate went into the benzene. The mercuric chloride left on evaporation of the benzene was determined by the Jamieson method.

Results

The results of the distribution experiments are given in Table I. The symbols used as column headings are explained on page 3585. Set A

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(9) Jamieson, "Volumetric Iodate Methods," 1926.

(10) Richards, THIS JOURNAL, **25**, 291 (1903).

(11) Findlay, "Practical Physical Chemistry," p. 113.

(12) Comey, "Dictionary of Solubilities," 1921.

TABLE I

The explanation of the column headings is given on page 3585. The averaged results of Experiments 1 and 2 are repeated under Sets B and C, in parentheses, for purposes of comparison.

No.	$\Sigma HgCl_2$	$\Sigma K_2C_2O_4$	$(HgCl_2)_b$	*a*	*b*	*x*	*y*	*z*	(Cl^-)	$(C_2O_4^=)$	*K′*
					Set A						
1	0.1069	0.0969	0.00619	0.0736	0.00161	0.0102	0.0083	0.00068	0.0115	0.0765	0.042
2	.1069	.0969	.00610	.0726	.00156	.0106	.0086	.00070	.0119	.0757	.051
3	.0713	.0969	.00408	.0485	.00070	.00790	.0050	.00027	.0105	.0811	.056
4	.0535	.0969	.00317	.0378	.00042	.00576	.0031	.00013	.0083	.0854	.039
5	.0356	.0969	.00213	.0254	.00019	.00410	.0016	.00005	.0065	.0887	.036
6	.0104	.0969	.000749	.00890	.000024	.00069	.00011	.000001	.00127	.0955	.0015
7	.0104	.0969	.000752	.00895	.000024	.00065	.00010	.000001	.00119	.0956	.0013
					Set B						
(1	.1069	.0969	.00615	.0731	.00159	.0104	.0085	.00069	.0117	.0761	.047)
8	.1065	.0495	.00678	.0806	.00193	.00734	.0062	.00056	.0079	.0348	.059
9	.1065	.0099	.00746	.0889	.00234	.0042	.0037	.00037	.0043	.0015	4.5
10	.1030	.00959	.00756	.0900	.00241	.0027	.0024	.00024	.0027	.0043	.134
					Set C						
11	.0609	.1412	.00328	.0390	.00045	.00810	.0044	.00019	.0116	.1250	.045
12	.0713	.1292	.00397	.0473	.00066	.00844	.0053	.00028	.0114	.1123	.039
(1	.1069	.0969	.00615	.0731	.00159	.0104	.0085	.00069	.0117	.0761	.047)
13	.1425	.0646	.00877	.1043	.00323	.0100	.0095	.0011	.0093	.0446	.042
14	.0535	.0485	.00373	.0444	.00059	.00298	.00178	.000088	.0041	.0425	.014
					Set D						
		$\Sigma(NH_4)_2C_2O_4$									
15	.0686	.1946	.00323	.0384	.00044	.0113	.0061	.00026	.0162	.1720	.068
16	.1236	.1168	.00644	.0765	.00174	.0147	.0122	.00104	.0162	.0874	.087

includes solutions in which the potassium oxalate concentration was constant; Set B, those in which the mercuric chloride concentration was constant; and Set C, those in which the concentrations were varied simultaneously, Experiments 11, 12, 1, 13, having the total salt concentration constant. Set D includes experiments with ammonium oxalate.

The ionic strengths of the solutions used in these experiments vary from 0.04 in No. 9 to 0.42 in No 11. Inasmuch as the ion activity coefficients are not well known for the higher values of the ionic strength, the correction of K' to K will not be made in the present paper. A rough calculation, however, shows that the value of K is approximately 0.1.

In Table II are presented the freezing point depressions of pure mercuric chloride and pure potassium oxalate solutions. The results for the potassium oxalate solutions by the Beckmann method are given uncorrected for the supercooling; in the final calculations this error cancels out. In each set of the table, the first column is the concentration in moles per liter, and the second column is the observed freezing point depression.

TABLE II

Mercuric chloride		Potassium oxalate					
		(Beckmann method)		(Richards method)		(Richards method)	
Concn.	ΔT	Concn.	ΔT	Concn.	ΔT	Concn.	ΔT
0.0485	0.089°	0.018	0.098°	0.0243	0.121°	0.110	0.499
.0623	.113	.054	.268	.0344	.166	.140	.627
.0778	.138	.108	.509	.0480	.232	.163	.728
.0920	.167	.180	.815	.0621	.293	.189	.841
.118	.209	.198	.896	.0848	.397		

TABLE III

(1) No.	(2) ($HgCl_2$) moles/liter	(3) ΔT_1[a]	(4) ($K_2C_2O_4$) moles/liter	(5) ΔT_2[b]	(6) Calcd. ΔT $\Delta T_1 + \Delta T_2$	(7) Obs. ΔT	(8) δ
B 1	0.180	0.325°	0.018	0.098°	0.423°	0.396°	0.027°
B 2	.162	.293	.036	.181	.474	.442	.032
B 3	.144	.260	.054	.268	.528	.493	.035
B 4	.117	.211	.081	.389	.600	.565	.035
B 5	.099	.178	.099	.470	.648	.617	.031
B 6	.090	.162	.108	.509	.671	.643	.028
B 7	.072	.129	.126	.588	.717	.688	.029
B 8	.054	.096	.144	.664	.760	.744	.016
B 9	.036	.064	.162	.740	.804	.798	.006
B 10	.018	.032	.180	.815	.847	.843	.004
R 11	.081	.147	.038	.183	.330	.317	.013
R 12	.073	.132	.068	.319	.451	.434	.017
R 13	.049	.089	.023	.112	.201	.194	.007
R 14	.048	.085	.088	.410	.495	.483	.012
R 15	.046	.083	.043	.209	.292	.284	.008
R 16	.053	.095	.049	.234	.329	.319	.010
R 17	.028	.050	.105	.482	.532	.530	.002

[a] Read from Curve II of Fig. 1. [b] Read from Curves III or IV of Fig. 1.

The results of freezing point determinations on Eder mixtures are given in Table III. Experiments by the Beckmann method are marked B; those by the Richards method are marked R.

It will be noticed that experiments 1 to 10 are for solutions of constant total molality. Figure 1 presents in graphical form the results in Table II, suitable for interpolation and use in Table III as explained.

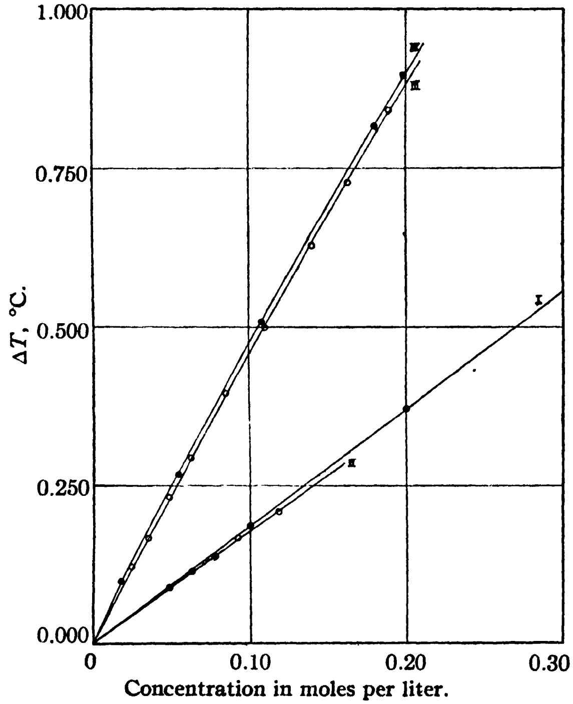

Fig. 1.—I, Theoretical non-electrolyte; II, mercuric chloride; III, potassium oxalate, Richards method; IV, potassium oxalate, Beckmann method.

The calculated values of δ are now compared in Table IV with the observed values from Column 8, Table III. The calculated values are found from Table I, from which (see page 3586) $\delta_{\text{calcd.}} = (1.86)(x + y + z)$.

Table IV

No. of expt.	$\delta_{\text{calcd.}}$	No. of expt.	$\delta_{\text{obs.}}$
Table I 1	0.036°	Table III 5	0.031°
Table I 3	.025	Table III 7	.029
Table I 4	.017	Table III 16	.010
Table I 5	.011	Table III 17	.002
Table I 6	.001	Table III 10	.004
Table I 11	.024	Table III 8	.016
Table I 12	.026	Table III 7	.029
Table I 13	.038	Table III 3	.035
Table I 14	.009	Table III 15	.008

Discussion

The results show that in the distribution experiments duplicate runs agree within about 1% in the measured concentration of mercuric chloride. On account of the subtractions involved in the calculations experimental errors are multiplied fifteen or twenty-fold in the final value of K'. Errors are introduced into K' also by the fact that the constants A and B are known to only two-place accuracy, and that the activity coefficients are not known. The calculations are least accurate when the oxalate-ion concentration is very low, as in Experiments 9 and 10 of Table I. Another factor that is beyond our control is the hydrolysis of the mercuric chloride. Considering only the experiments in which neither component is present in greater than three to one excess over the other, the values of K' show no drift as the concentration ratio is varied, whereas decided drifts are obtained when other schemes of formulation are tried. Thus, if we arrange the significant experiments of Table I in order of decreasing ratio of bichloride to oxalate, taking average values of K' for runs having approximately equal ratios of the formalities, we obtain the values of K': 0.050, 0.047, 0.056, 0.039, 0.045, 0.036, when $\Sigma HgCl_2/\Sigma K_2C_2O_4$ varies from 2.2 to 0.37. According to scheme 4 (page 3585) the corresponding values of the constant are: 9.5, 6.3, 5.8, 4.6, 4.5, 4.4. When the concentration ratio differs widely from unity it is most likely that the composition of the complex changes, as is known to be the case with the chloro complexes.

The agreement between the calculated and observed values of δ (Table IV) is also satisfactory, these being obtained from differences of measurements which are hardly accurate to more than 0.003°. Furthermore, these values are compared in solutions of only approximately the same composition and, of course, at two different temperatures, 0 and 25°. Thermal effects, however, on solutions of this type of complex should be relatively small in the neighborhood of room temperature. The observed values of δ are all less than would be expected if the complex had the formula $HgCl_3C_2O_4^{-}$.

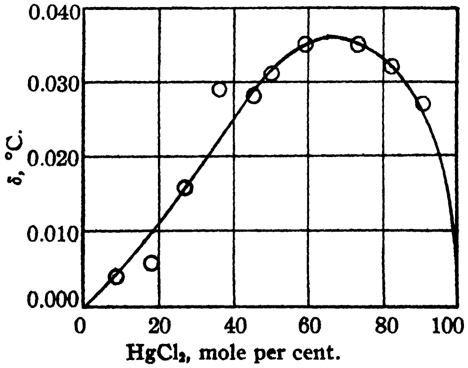

Fig. 2.

The variation in the value of δ with the ratio of bichloride to oxalate in solutions whose gross formality is constant is particularly striking. This variation is shown graphically in Fig. 2, from which it is evident that the greatest decrease in the freezing-point lowering occurs with an excess of bichloride. This is undoubtedly due to the effect of the mercuric chloride in forming chloro complexes, which is to be expected from a formulation such as the one here proposed, but not if the complex is formed by the reaction $HgCl_2 + C_2O_4^{=} \rightleftharpoons HgCl_2C_2O_4^{=}$ in which no chloride ions are liberated.

The scheme of complex formation presented on page 3585 is thus in good agreement with experiment, such an agreement not being found for any of the other formulations which were tried. It will be convenient to remember that in the original Eder solution, as usually made up (Expt. 15, Table I), the concentration of the complex $Hg_2Cl_2(C_2O_4)_2^{=}$ is approximately 0.01 molar.

Discussion of the Rate of the Eder Reaction.—The mercuri-oxalate complex which has been shown to exist in Eder's solution may be made the basis of an explanation of the reaction rate measurements.

Roseveare,[13] Roseveare and Olson,[14] and Wyckoff and Baker[15] have found that the rate of Eder's reaction is proportional to the first power of the mercuric chloride concentration under certain conditions. This is to be expected from a consideration of the equilibrium equation. If we assume that no excess of chloride ion is initially present, the formation of a complex mercuri-chloro-oxalate ion liberates two chloride ions, so that, as a first approximation, the chloride-ion concentration is twice the concentration of the complex ion. We have, therefore

$$\begin{aligned}(Hg_2Cl_2(C_2O_4)_2^{=}) &= K(HgCl_2)^2(C_2O_4^{=})^2/(Cl^-)^2\\ &= K(HgCl_2)^2(C_2O_4^{=})^2/4(Hg_2Cl_2(C_2O_4)_2^{=})^2\end{aligned}$$

from which, for a given oxalate concentration, $(Hg_2Cl_2(C_2O_4)_2^{=}) \propto (HgCl_2)^{2/3}$. Since our measurements show that, within limits, the free $HgCl_2$ is proportional to the total mercury present (Expts. 1 to 5, Table I), in the early stages of the decomposition reaction the rate should be roughly proportional to somewhat less than the first power of the concentration of mercuric chloride. This was found to be the case for both the thermal and x-ray photolytic reactions. When chlorides are initially present the order of the reaction as to mercuric chloride should increase, according to our formulation. This appears to be the case, since the results of Roseveare and Olson (Ref. 14, Tables II and III) agree better with a second order equation than with a first order one when considerable potassium chloride is present. The presence of high concentrations of chlorides so complicates the problem, however, that we cannot be certain what the results mean. It appears most likely that the composition of the mercuri-chloro-oxalate complex changes when chlorides are present in considerable concentration. Not only so, but the kinetic relationships are also complicated by salt effects quite apart from the specific action of the chloride ions, as has been shown for Eder's reaction by Berger.[4]

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(13) Roseveare, THIS JOURNAL, **52**, 2617 (1930).

(14) Roseveare and Olson, *ibid.*, **51**, 1716 (1929).

(15) Wyckoff and Baker, *Am. J. Roentgenol. Radium Therapy*, [6] **22**, 551 (1929).

Particularly interesting results are obtained, however, when we consider the order of the reaction with respect to oxalate ion. Roseveare and Olson found that the rate varies as the second power of the oxalate-ion concentration in the absence of oxygen, but in two experiments run with the solutions saturated with oxygen, the reaction became first order with respect to the oxalate concentration. Likewise; Roseveare found a first-order rate with respect to oxalate in the x-ray photolysis in the *absence* of oxygen. Dhar[16] also found the reaction to be monomolecular as to both mercuric chloride and potassium oxalate with no chloride added and with an indefinite concentration of oxygen (solutions previously saturated with carbon dioxide). These conflicting results are clarified by considering the different conditions under which the rates were measured.

From our equilibrium equation $(Hg_2Cl_2(C_2O_4)_2^{=}) = K(HgCl_2)^2(C_2O_4^{=})^2/(Cl^-)^2$, the reaction rate with respect to the oxalate concentration should have different values according as the chloride ion accumulates during the reaction or else remains more or less fixed. As previously pointed out (page 3592, *et seq.*), if no chloride ion is initially present the concentration of the complex ion varies as $(HgCl_2)^{2/3}(C_2O_4^{=})^{2/3}$, or, the initial reaction rate should be less than first order with respect to oxalate. This situation prevails when the mercury is not present in considerable excess and no potassium chloride is added; under these conditions, the initial chloride-ion concentration is equal to twice the concentration of the complex. Now these are exactly the conditions under which the oxygen experiments of Roseveare and Olson and the x-ray photolysis of Roseveare were carried out. On the other hand, if chloride ion is added to the reaction mixture, the additional chloride ion liberated in the formation of the complex is inappreciable and the concentration of the complex varies as the square of the oxalate-ion concentration. Also, if no potassium chloride is added but mercuric chloride is used in considerable excess, the chloride ion initially liberated is extensively removed by the formation of chloro complexes, so that in this case also the rate should vary as the square of the oxalate ion concentration.

From the results of our distribution experiments it is uncertain whether the same mercuri-chloro-oxalate complex persists as the oxalate–mercury ratio deviates widely from unity, but it is significant that the kinetic measurements reveal just the variation in reaction order that our formula leads us to expect. If the formula were $HgCl_2C_2O_4^{=}$, as proposed by Roseveare, the maximum concentration of complex for a given total salt concentration should occur when the mercuric chloride and potassium oxalate were present in equimolal proportions; whereas, according to our measurements, the maximum formation of complexes occurs on the mercuric chloride side of metathetical equivalence.

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(16) Dhar, *J. Chem. Soc.*, **111**, 690 (1917).

Summary

1. The results of experiments on the partition of mercuric chloride between aqueous potassium oxalate and benzene are presented.

2. The freezing point depressions of mercuric chloride and of potassium oxalate solutions and of mixtures of these have been determined.

3. It is shown that calculations from the distribution and freezing point experiments lead to the following scheme of complex formation in Eder's solution:

$$2HgCl_2 + 2C_2O_4^{=} \rightleftarrows Hg_2Cl_2(C_2O_4)_2^{=} + 2Cl^-$$
$$HgCl_2 + Cl^- \rightleftarrows HgCl_3^-$$
$$Hg_2Cl_4 + Cl^- \rightleftarrows Hg_2Cl_5^-$$

4. This scheme is shown to be in harmony with reaction rate measurements on Eder solutions over a corresponding range of concentrations.

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A Study of Polarization Currents Due Solely to Changes in Electrode Area[1]

BY KENNETH E. GLIDDEN[2] AND W. A. PATRICK

Introduction

The purpose of this investigation was to study the adsorption of mercurous ions at a mercury surface by measuring the current flowing between two mercury electrodes immersed in a mercurous sulfate solution while one of the electrodes was undergoing a slow definite increase in area. Similar studies have been made in the past, but always under conditions that made the interpretations of results quite difficult.

Heyrovský and co-workers have used the dropping mercury electrode to investigate a variety of chemical problems. Semerano gives a discussion of the work of these investigators using the polarograph, an instrument for the automatic recording on photographic paper of the current-voltage curves obtained with the dropping mercury cathode.[3] Frumkin and Schofield[4] have used the dropping mercury electrode to verify the Lippmann equation. Frumkin measured the current caused by a stream of mercury drops falling through the various solutions used, while Schofield actually measured the amount of mercurous salt which was removed from a solution by an expanding mercury surface.

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(1) From a dissertation submitted by K. E. Glidden to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the Doctor of Philosophy Degree, June, 1932.

(2) Brown Company Fellow in Chemistry.

(3) Semerano, "Il Polarografo, sua Teoria e Applicazioni" (The Polarograph, Its Theory and Applications), Libreria Editrice A. Draghi, Padova, Italy, 1932.

(4) Frumkin, *Z. physik. Chem.*, **103**, 55 (1922); Schofield, *Phil. Mag.*, **1**, 641 (1926).

All the dropping electrode experiments, in regard to the adsorption at the expanding surface, are ambiguous due to the rapid formation of mercury drops in the solution with the subsequent changes of metal ion concentration at the electrode surface. Furthermore, the change of solute concentration thus produced causes a change of interfacial tension, which in turn causes a variation in the size of the drops. If we add to the above objections the possibility of a slow rate of surface orientation at the electrode surface, it is evident that most dropping electrode experiments are complicated phenomena that defy analysis.

The fundamental assumption in this paper is that the adsorption of mercurous ions is equivalent to the current measured. It is an experimental fact that a rain of mercury drops falling through a solution containing for example lead ions does not adsorb lead ions from solution, and hence it appears that we are dealing with specific adsorptive forces rather than purely electrostatic forces. At the present time there is no direct evidence that our fundamental assumption is correct. The fact that the adsorption of mercurous ions calculated from our polarization current measurements on the basis of the above assumption agrees fairly well with the adsorption obtained from an entirely different method, leads us to believe that our fundamental assumption is reasonable.

Apparatus

The currents were produced with the apparatus shown in Fig. 1. The slowly expanding surface consisted of a mercury drop on the tip of a ground and polished capillary tube *a*, 1.41 millimeters in diameter. The fixed surface electrode *b* was made by sealing a 1-cm. tube through the wall of the cell *c*. The cell was cylindrical in shape, approximately 8 by 50 cm. The area of the mercury drop in contact with the solution was increased by adding mercury to the main reservoir *d* from the auxiliary reservoir *e*. The cross sectional area of the main reservoir was approximately 800 times that of the capillary bore, and hence if dV_c is the volume increase of the mercury drop produced by a volume increase dV_r at the reservoir, dV_c is approximately equal to $dV_r/800$.

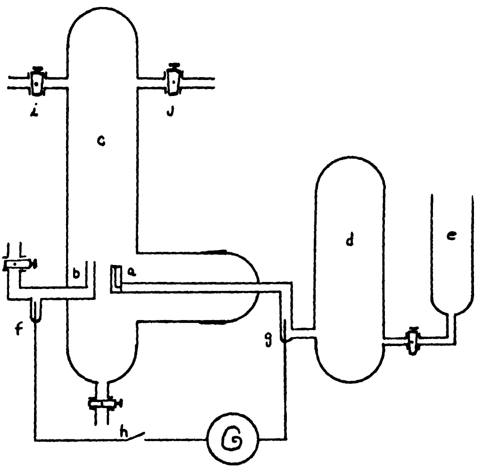

Fig. 1.—Diagram of apparatus (scale: 1 in. = 20 cm.).

Tungsten wires were sealed in the electrodes at *f* and at *g* and connected to the poles of a Leeds and Northrup galvanometer as shown in the diagram. A switch *h* was employed to open and close the circuit. The entire apparatus was supported on hard rubber or bakelite to eliminate current leakage.

The drop was observed with a cathetometer telescope containing a calibrated screw micrometer eyepiece. A lens was placed between the telescope and object to increase the magnification.

Experimental

Introduction of Solution into Cell.—The entire cell was evacuated through the stopcock at *i* with a mercury diffusion pump backed by an oil pump. Carefully purified mercury was then added through the auxillary reservoir *e* until the level of the mercury in the capillary electrode was just at the tip. The level in *b* was likewise adjusted by adding mercury through a stopcock provided for that purpose.

A stock solution of mercurous sulfate was prepared by saturating distilled water with C. P. mercurous sulfate. A small amount of mercury was kept in contact with the solution to prevent the formation of mercuric salts. After standing in contact with solid mercurous sulfate for ten days or more, the solution was filtered and analyzed for mercury by electrolysis. The stock solution is of course acid due to hydrolysis, but the exact acidity was unknown.

A bulb of about 250 cc. capacity (not shown in the diagram) joined to stopcock *j* was then filled with a solution of mercurous sulfate, which was prepared by diluting the stock mercurous sulfate solution with boiled distilled water which had been cooled rapidly to prevent absorption of oxygen from the air. Stopcock *j* was then opened slightly to allow a trickle of solution to enter the polarization cell. During this process practically all of the dissolved gases are drawn out of the solution and removed from the system by the pumps. If the flow of solution from the bulb to the cell does not exceed 150 cc. per hour, the de-aerated solution will contain not more than 10^{-5} cc. of oxygen per 100 cc. of solution. The stopcock at *i* was opened for thirty seconds every five minutes to draw off air removed from the solution. Solution was added to the cell through the bulb until a total of 1000 cc. had been added. Since a great deal of water is lost through the pumps during the de-aeration process, boiled distilled water which had been cooled rapidly was added to the cell through the de-aerator until the total volume of solution was 1000 cc.

To change the concentration in the cell, a pear-shaped bulb was sealed on at *j*. This bulb was evacuated, sealed off from the pumps and cooled with a mixture of solid carbon dioxide and ether. Stopcock *j* was then opened and water from the cell allowed to distil over, approximately six to eight hours being required to distil over 100 cc. The initial concentration of mercurous sulfate solution in the cell was known and hence the successive concentrations could be estimated by weighing the amounts of water removed by distillation.

Current Measurements.—The procedure followed in the current measurement was as follows. The flow of mercury from the auxiliary to the main reservoir was adjusted to such a rate that the meniscus of the mercury drop on the capillary tip passed between two cross hairs in the telescope eyepiece in 120 ± 5 seconds. The switch *h* was thrown as the meniscus passed the first cross hair, and the galvanometer deflection read every ten seconds for the entire time interval. The above procedure was repeated several times for each particular concentration of mercurous sulfate solution in the cell.

Area Measurements.—The optical system for viewing the drop was not sufficiently sensitive to detect the area change over an interval of ten or fifteen seconds, and hence the average rate of change over the one hundred twenty second interval was measured.

The area of a segment of a sphere is $2\pi rh$ where r is the radius of the sphere and h the height of the segment. The radius of the drop on the capillary tip is not the same as the radius of the capillary and it varies with the height of the drop above the tip. Assuming that the drop is spherical, the average rate of change of mercury surface in contact with solution may be calculated as follows. Let h_0 be the height of the meniscus above the tip of the capillary at time 0; h_t the height after t seconds; r_0 and r_t the radii of curvature of the drop at the two positions; S_0 and S_t the areas of the segments; and a the radius of the capillary. Then $r_0^2 = a^2 + (r_0 - h_0)^2$ and $r_0 = (a^2 + h_0^2)/2h_0$. A similar expression for r_t in terms of h_t and a may also be written. Since $S_0 = 2\pi r_0 h_0$ and $S_t = 2\pi r_t h_t$ it follows that

$$\frac{\Delta S}{\Delta t} = \frac{S_t - S_0}{t - 0} = \frac{2\pi(r_t h_t - r_0 h_0)}{t - 0} = \frac{\pi(h_t^2 - h_0^2)}{\Delta t}$$

This final expression gives the average rate of change of mercury surface in contact with solution during the time interval considered, and if the total area change is small, the average rate does not differ greatly from the instantaneous rate.

Experimental Results

The data obtained for seven concentrations of mercurous sulfate solution in which the electrodes were immersed are summarized in Table I. The first column lists the concentration of mercurous sulfate solution in millimoles per liter; the second gives the average rate of change of mercury surface in contact with solution, expressed in square centimeters per second; the third column gives the actual current in amperes flowing between the electrodes, these values computed from the observed galvanometer deflections and the galvanometer sensitivity; the fourth column lists the adsorption per unit time, these values calculated from the current measurements and the factor 2.07×10^{-3} g. of mercurous ion per coulomb, and expressed in grams of mercurous ion per second; the final column gives the adsorption per unit surface, expressed in grams of mercurous ion per square centimeter of mercury surface. These values were calculated by dividing the adsorption per unit time by the change of mercury surface per unit time. All the values in Table I represent the mean of twenty or more individual measurements. The total area change in all cases was 0.00391 square centimeter.

TABLE I

Concn.	$\Delta S/\Delta t$	Current	Adsorp./sec.	Adsorp./sq. cm.
0.091	3.30×10^{-5}	2.22×10^{-9}	46.0×10^{-13}	0.14×10^{-6}
.093	3.22	2.80	58.0	.18
.100	3.35	3.72	77.0	.23
.131	3.20	5.27	109.0	.34
.157	3.21	5.50	113.0	.35
.203	3.31	5.36	111.0	.33
.302	3.20	5.38	111.5	.34

A plot of the values of adsorption of mercurous ion per square centimeter against concentration of mercurous sulfate solution is shown in Fig. 2.

Discussion of Results

These experiments were undertaken with a view to ascertaining whether or not these small currents could throw any light on the extent of ion orientation at the electrode surface. Experiments performed by Seidel in which he employed the micro-balance to measure the extent of mercurous ion adsorption at mercury surfaces, indicated that a unimolecular layer was formed at a concentration of 0.13 millimole of mercurous sulfate per liter.[5] Above this concentration no further increase in adsorption was detectable notwithstanding the fact that the interfacial tension between mercury and solution continued to diminish. The adsorption calculated from the polarization currents reported in this paper substantiates the results obtained by Seidel, especially in regard to the constancy of adsorption above a certain critical value of mercurous sulfate solution concentration. The actual value for the adsorption of mercurous ion per unit surface is of the same order of magnitude from both methods, that from the polarization current measurements being one-third that obtained from the micro-balance measurements.

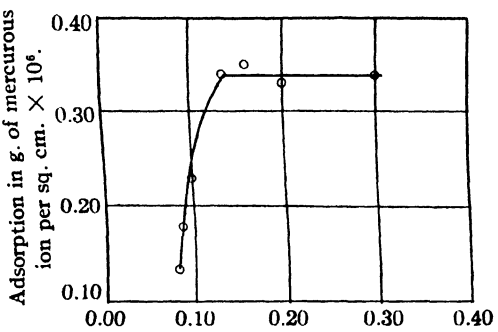

Fig. 2.—Adsorption curve for mercurous ions at a mercury surface.

The Gibbs adsorption equation for an ideal solute may be stated as follows:

$$u = -1/RT\ \partial\sigma/\partial \ln c \quad (1)$$

u being the number of moles of solute adsorbed per unit surface, σ the interfacial tension, c the bulk concentration, R and T having the usual significance.

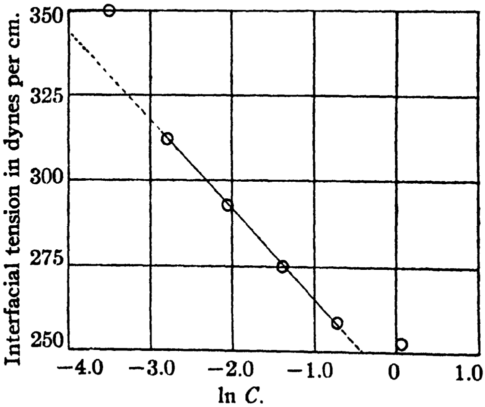

Fig. 3.—Surface tension–ln C curve for Hg–Hg_2SO_4.

From equation (1), it is evident that the condition for a constant value of positive adsorption is that the interfacial tension decrease linearly with the logarithm of the concentration. Patrick's data on the interfacial tension between mercury and mercurous sulfate solution show that the relationship is linear

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(5) Seidel, Dissertation, the Johns Hopkins University, June, 1931.

from a concentration of 0.13 to 0.50 millimole of mercurous sulfate per liter, and that deviations occur in dilute or concentrated solutions. These data are shown in Fig. 3.[6]

A thermodynamic interpretation of equation (1) may be obtained by the following considerations. Assume an interface of area ω, interfacial tension σ, in contact with a solution of osmotic pressure p and volume v. A small change of area $d\omega$ results in the following change of internal energy

$$dU = TdS + \sigma d\omega - pdv \qquad (2)$$

σ is by definition the work required per unit increase of surface, and hence the term $\sigma d\omega$ represents the increase in the free energy of the system. TdS and pdv are, respectively, the heat absorbed and the volume work performed when the area of the interface is increased by $d\omega$.

The free energy (F) is defined as

$$F = H - TS = U + pv - TS \qquad (3)$$

This expression is differentiated and combined with equation (2), and at constant temperature the following expression is obtained

$$dF = \sigma d\omega + vdp \qquad (4)$$

By applying the criterion for equilibrium, *i. e.*, $dF = 0$, we obtain

$$\sigma d\omega = -vdp \qquad (5)$$

This equation shows that with an increase $d\omega$ of the interface, the change in free surface energy is exactly equal to the osmotic work performed in the process.

By differentiating equation (5) and neglecting all differentials of higher order than the first, we obtain

$$d\sigma d\omega = -dv\, dp \qquad (6)$$

This equation may be written as

$$\left(\frac{\partial\sigma}{\partial v}\right)_\omega = -\left(\frac{\partial p}{\partial \omega}\right)_V \quad (7a) \qquad \text{or} \qquad \frac{\partial\sigma}{\partial c}\frac{\partial c}{\partial v} = -\frac{\partial p}{\partial c}\frac{\partial c}{\partial \omega} \quad (7b)$$

All of the coefficients in (7b) with the exception of $\partial\sigma/\partial c$ may be evaluated from the osmotic pressure law for an ideal solute, and the Gibbs definition of concentration.

$$p = cRT \quad (8) \qquad c = (n - u\omega)/v \quad (9)$$

In equation (9), c gives the bulk concentration, n the total number of moles of solute, v the total volume, ω the total surface and u the adsorption coefficient of the constituent in the surface layer. If an increase of surface decreases the concentration of one constituent in the body of the solution, that constituent is said to be adsorbed at the surface. Hence u represents the excess of the adsorbed constituent in the surface layer above that required to give the surface layer the same composition as the body of the solution.

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(6) Patrick, *Z. physik. Chem.*, **86**, 545 (1914).

An evaluation of the coefficients in equation (7b) results in the Gibbs adsorption equation for an ideal case. We have seen that the sole condition for a constant value of adsorption is that the intensity factor of the surface energy, the interfacial tension, decrease linearly with the logarithm of the solute concentration. In spite of the fact that Patrick's data on the interfacial tension between mercury and mercurous sulfate solution show that this condition is fulfilled (within a certain range of concentration), the authors believe it worth while to present a modification of the Gibbs theory.[6]

If one accepts the fact that above a certain critical concentration no further increase in adsorption occurs, it is necessary to account for the continued lowering of the free surface energy. Our contention is that this lowering is due entirely to the orientation of electrically charged particles at the surface. In other words, the free surface energy lowering only occurs through the mechanism of orientation, and this oriented surface layer is the seat of a definite amount of electrical energy which is governed primarily by the geometry of the surface particles.

We now define concentration in terms of an oriented unimolecular layer of adsorbed particles as follows

$$c = (n - q/NF)/v \tag{10}$$

q being the total charge at the surface, NF the number of coulombs associated with a mole of surface particles, n the total number of moles and v the total volume. The ratio q/NF hence gives the number of moles of solute particles absorbed at the surface.

With an interface of area ω, interfacial tension σ, surface charge q, surface potential ϵ, in contact with a solution of osmotic pressure p and volume v, a change of area $d\omega$ results in the following change of internal energy

$$dU = TdS + \epsilon dq - pdv \tag{11}$$

This equation is identical with the fundamental equation in the derivation of the Gibbs equation with the exception that an electrical energy term (ϵdq) replaces the term ($\sigma d\omega$) for the lowering of the free surface energy. ϵ is the intensity factor in the electrical energy term which is comparable to the intensity factor σ in the surface energy term of equation (2).

The free energy expression (3) is then differentiated and combined with (11)

$$dF = \epsilon dq + vdp \quad \text{(at constant temperature)} \tag{12}$$

By applying the criterion for equilibrium, $dF = 0$, differentiating and neglecting all differentials of higher order than the first, we obtain

$$d\epsilon\, dq = -dv\, dp \tag{13}$$

This equation may be written as

$$\left(\frac{\partial\epsilon}{\partial p}\right)_q = -\left(\frac{\partial v}{\partial q}\right)_p \quad \text{(14a)} \qquad \text{or} \qquad \frac{\partial\epsilon}{\partial c}\frac{\partial c}{\partial p} = -\frac{\partial v}{\partial c}\frac{\partial c}{\partial q} \quad \text{(14b)}$$

The coefficients appearing on the right-hand side of (14b) may be evaluated from the definition of concentration previously stated, equation (10); $\partial c/\partial p$ may be found from the osmotic pressure law for an ideal solute. If one regards the adsorbed layer as a double electric layer, the question immediately arises as to how the potential of such a combination varies with the solute concentration. We postulate that the potential of the surface layer will vary with the solute concentration according to the usual thermodynamic relationship

$$\epsilon = (RT/NF) \ln c \tag{15}$$

An evaluation of the coefficients in (14b) leads to the identity

$$\frac{RT}{NF}\frac{1}{c}\frac{1}{RT} = \frac{v}{c}\frac{1}{NFv} \text{ or } 1 = 1 \tag{16}$$

This final step shows that the argument presented above is thermodynamically correct.

It now remains to show that the decrease of free surface energy between mercury and mercurous sulfate solution with increasing solute concentration is of an order of magnitude to be accounted for by the formation of an oriented unimolecular layer of solute particles. The problem may best be attacked by considering the adsorbed layer as a parallel plate condenser.

The capacity of a single parallel plate condenser may be calculated from its geometry, *i. e.*, the area of the plates and the distance of separation; capacity is also related to the charge and potential of the plates. These relationships are shown in the expression

$$C = K\omega/4\pi d = q/e \tag{17}$$

In order to simplify the calculation, we will assume that the radius of the cation and anion are the same, and hence in the above expression, $d = 2r$. If ω is the area occupied by one charged particle of radius r, the capacity then becomes

$$C = K\pi r^2/8\pi r = Kr/8 \tag{18}$$

Since the mercurous ion bears two unit charges, the potential of the double layer becomes

$$\epsilon = 16/Kr \tag{19}$$

The charge per square centimeter may be obtained by multiplying the number of surface particles per square centimeter by the charge of each surface particle, hence

$$q/cm^2 = 1/\pi r^2 \quad 2 \times 9650/N \quad \text{e. m. u.} \tag{20}$$

Since electrical energy is the product of charge and potential, the energy associated with one square centimeter of surface is given by the expression

$$\epsilon \cdot q = 16/Kr \quad 2 \times 9650/N\pi r^2 = 16.2 \times 10^4/Kr^3 \tag{21}$$

This final expression for the energy is given in ergs per square centimeter if r is expressed in Ångström units, and shows that the energy associated with the surface layer depends primarily on the geometry of the surface particles.

In order to make the calculation for the electrical energy per unit surface, the dielectric constant K and r must be known. The value of r may be calculated from the experimental value of the adsorption of mercurous ion, 0.34×10^{-6} g. of mercurous ion per square centimeter of mercury surface, and is found to be 2.5 Å. The dielectric constant of the oriented layer is unknown but will very probably be close to that of water.

Using the values $K = 81$ and $r = 2.5$ Å., the energy per square centimeter of an oriented unimolecular layer of mercurous sulfate particles is found to be approximately 120 ergs.

Since we have postulated that the lowering of the free surface energy is due entirely to the formation of an oriented unimolecular layer of solute particles, it is evident that the lowering of the interfacial tension between mercury and mercurous sulfate solution must be of the same order of magnitude as the energy required to form this surface layer. Patrick's data for the interfacial tension between mercury and mercurous sulfate solution show that the lowering from 0.13 to 1.03 millimole of mercurous sulfate per liter (the approximate region in which we postulate a unimolecular layer of solute particles) is 42 ergs per square centimeter. Since our calculation for the electrical energy associated with one square centimeter of surface involves many questionable assumptions, the agreement between the two values is all that can be expected.

Summary

1. The current flowing between a fixed and expanding mercury surface, both surfaces in contact with a mercurous sulfate solution, has been measured. On the assumption that the current measured is equivalent to adsorption of mercurous ions, the adsorption of mercurous ions is constant above a certain critical solute concentration.

2. The lowering of the interfacial tension between mercury and mercurous sulfate solution can be accounted for by the formation of an oriented unimolecular layer of mercurous sulfate particles at the mercury surface.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Calcium Nitrate. IV. Heats of Dilution of Solutions of Calcium Nitrate in Water

BY WARREN W. EWING AND ALFRED N. ROGERS

If n_2 moles of solute are dissolved in n_1 moles of water giving a solution of concentration m, the increase in heat content, ΔH, is a measure of the heat absorbed by the reaction. This is called the total or integral heat of solution. If n_2 moles of solute are dissolved in such a large volume of solution of concentration m that there is no change in concentration, the increase in heat content, $n_2\Delta\text{H}_2$ is called the partial, or differential, heat of solution of the solute. Similarly, if n_1 moles of water are dissolved in such a large volume of solution that there is no change in concentration, $n_1\Delta\text{H}_1$ is termed the partial, or differential, heat of solution of water in the solution. These quantities are related by the equation

$$\Delta H = n_2\Delta\text{H}_2 + n_1\Delta\text{H}_1 \qquad (1)$$

where ΔH_2 and ΔH_1 are the partial molal heats of solution of solute and solvent, respectively. If ΔH is known at several concentrations, ΔH_2 can be evaluated by determining the slope of the curve obtained by plotting ΔH against m. ΔH_1 can then be evaluated by means of equation (1). ΔH_1 can also be calculated from vapor pressure data if the vapor pressures of the solutions are known at two temperatures. In this article, the determinations of the partial heat of solution of water in calcium nitrate solutions from calorimetric data and from vapor pressure data are presented.

Previous studies on heats of dilution in concentrated solutions have been made by a few workers, notably by Randall and Bisson[1] on sodium chloride solutions; and by Harrison and Perman[2] on calcium chloride and potassium chloride solutions; but the solubility of the substances studied had only a limited range, the highest concentration of sodium chloride, for example, being only 6.12 molal. The concentration of a saturated solution of calcium nitrate anhydride in water at 25° is 77.3%, or 20.75 moles in 1000 g. of water. At this concentration, the solution is supersaturated with respect to the dihydrate, the trihydrate and the tetrahydrate. The solution is stable enough that it can be kept for long periods of time, however; and it withstands considerable experimental manipulation without crystallizing. Solutions of calcium nitrate, therefore, serve as systems on which heat of dilution studies can be carried out over a very large range of concentrations.

Randall and Bisson[1] and MacInnes and Braham[3] have measured ΔH_1 directly by dissolving small quantities of water in large volumes of solution.

(1) Randall and Bisson, THIS JOURNAL, **42**, 347 (1920).

(2) Harrison and Perman, *Trans. Faraday Soc.*, **23**, 1 (1927).

(3) MacInnes and Braham, THIS JOURNAL, **39**, 2110 (1917).

This procedure was not feasible with calcium nitrate solutions because the concentrated solutions were both viscous and in a metastable condition. When small quantities of water were added to the viscous solution, it was difficult to obtain uniform distribution. There was also danger that the manipulation in the calorimeter would disturb the metastable equilibrium whereupon the whole solution would crystallize. The procedure followed was to dissolve small quantities of solution in 1000 g. of water. These heats of dilution could be calculated to infinite dilution since Lange and Streeck[4] have measured heats of dilution of calcium nitrate solutions from one-tenth molal to infinite dilution. From these heats of dilution and the heat of solution of calcium nitrate anhydride, the quantities involved in equation (1) can be calculated.

Experimental

The apparatus used has been described in a previous article.[5] The only alteration was the replacement of the mercury-in-glass thermometer by a platinum resistance thermometer. This thermometer was of the knife blade type, made by Leeds and Northrup, and calibrated at the Bureau of Standards. The resistance of this thermometer was measured by means of a Mueller type temperature bridge, made by the Eppley Laboratory, Inc. The resistances of this bridge were immersed in oil, of which the temperature was maintained constant by a thermostatic control. Resistances could be measured to 0.0001 ohm, and estimated to 0.00003 ohm. This gave temperature differences accurate to 0.0005°.

In each run four small sealed bulbs containing a calcium nitrate solution of known concentration were placed in the calorimeter containing 1000 g. of water. The solution

TABLE I

HEATS OF DILUTION AND OF SOLUTION

	Orig. concn.		Total heat of dilution ΔH in joules per mole $Ca(NO_3)_2$				Total heat of solution	
	Moles per 1000 g. H_2O, m	n_2/n_1	Run 1	Run 2	Run 3	Av.	1 mole $Ca(NO_3)_2$ in req. amt. H_2O	m moles $Ca(NO_3)_2$ in 1000 g. H_2O
1	2	3	4	5	6	7	8	9
$Ca(NO_3)_2$	0.01	0.0002				− 640[a]	−18,610	− 186
	.1	.0018				− 900[a]	−18,350	− 1,835
	1.393	.0244	+2488	+2507	+2442	+2479	−21,729	− 30,269
	2.552	.0460	+4111	+4124	+4152	+4129	−23,379	− 59,663
	3.96	.0714	+5036	+5000		+5018	−24,268	− 96,101
	4.03	.0726	+5027	+5055	+5066	+5049	−24,299	− 97,925
	6.73	.1213	+4487	+4492	+4492	+4490	−23,740	−159,750
	8.08	.1456	+3666	+3676	+3676	+3673	−22,923	−185,218
	10.65	.1919	+1964	+1952	+1938	+1951	−21,201	−225,790
	13.85	.2495	− 284	− 190	− 327	− 267	−18,983	−262,915
	19.55	.3595	−3423	−3427	−3447	−3432	−15,818	−309,241
$Sr(NO_3)_2$	1.147	.0207	+4371	+4550	+4490	+4470	+13,070	+ 14,991
	1.985	.0358	+7257	+7193	+7233	+7228	+10,312	+ 20,469
	3.123	.0563	+9571	+9599	+9543	+9571	+ 7,969	+ 24,887

[a] Values of Lange and Streeck, Ref. 4.

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(4) Lange and Streeck, *Z. physik. Chem.*, **157A**, 15 (1931).

(5) Ewing, Rogers, Miller and McGovern, THIS JOURNAL, **54**, 1335 (1932).

was introduced into the water by breaking the bulbs and the temperature change accurately measured. From this temperature change and the heat capacity of the calorimeter, the changes in heat content were calculated. The data are given in Table I. Also data for strontium nitrate solution are included in this table. These results for strontium nitrate will be discussed when vapor pressure measurements, which are now being made, are completed. Column 7 contains the change in heat content when one mole of calcium nitrate contained in a solution of the concentration designated in Column 2 is diluted in enough water to give infinite dilution. These heats were plotted against concentration in Curve I, Fig. 1.

Accuracy of Results.—Applying the equations of the theory of errors to our results, we find that the root mean square deviation is 43.5 joules. The probable error of any observation is 0.6745 × 34.5 = 29.3 joules. It is immediately obvious, however, that this is not a true measure of the accuracy, for the "spread" or maximum deviation of the results for any particular solution varies from 5 to 179 joules. The deviations can be accounted for as follows.

The heat capacity of the calorimeter and its contents was determined for each individual heat determination by passing a known current I through a resistance R inside the calorimeter for a time t. The heat evolved, RI^2t, caused a rise in temperature ΔT, the heat capacity being obtained from the relation

$$C = Q/(\Delta T) = RI^2t/(\Delta T)$$

Now the error in Q is

$$\Delta Q = RI^2\Delta t + 2RIt\Delta I + I^2t\Delta R$$

Since I and R can be measured with great precision, the second and third terms are negligible. This leaves us

$$\Delta Q = RI^2\Delta t = 17.07 \times (0.444)^2 \times 0.4 = 1.346 \text{ joules}$$

Here, we are assuming a probable error of 0.4 second in the heating interval due to closing and opening of the heater switch. Now

$$\Delta C = \frac{\Delta Q}{(\Delta T)} - \frac{Q}{(\Delta T)^2}\Delta(\Delta T)$$

or for the *probable* error in C

$$\text{probable } \Delta C = \sqrt{\left(\frac{\Delta Q}{\Delta T}\right)^2 + \left[\frac{Q}{(\Delta T)^2}\Delta(\Delta T)\right]^2} =$$

$$\sqrt{\left(\frac{1.346}{0.59}\right)^2 + \left[\frac{2600}{(0.59)^2}(0.00045)\right]^2} = \pm 4.1 \text{ joules per } 1^\circ$$

As stated before, the temperature could not be estimated more closely than 0.0003°. A temperature change, therefore, may be in error by as much as 0.0006°. A probable error of 0.00045° was considered a fair estimate of the precision of the temperature measurement This is the value used in obtaining ΔC above.

The error in heat capacity together with the temperature error when combined by a process similar to the above, produces an error in heat of dilution. In order to convert the latter into joules per mole of dry salt, we must multiply by a factor depending on the original concentration of the solution, the weight of the solution diluted, and the molecular weight of the salt in question. The resulting probable error ranges from 86.2 joules per mole $Sr(NO_3)_2$ for the 19.5% $Sr(NO_3)_2$ solution down to 15.8 joules per mole $Ca(NO_3)_2$ for the 69.5% $Ca(NO_3)_2$ solution. In general, our calculations show that the lower the original concentration, the higher the probable error. This conclusion is corroborated by our observations.

Discussion

These heat data can be compared with vapor pressure data by thermodynamic methods. In order to do so, it is necessary to calculate them on a different basis. The values required are the partial molal heats of solution of water, $\Delta \mathrm{H}_1$, in the solutions of various concentrations. These can be calculated from the above data and the total heat of solution of calcium nitrate anhydride. The latter value has been given in a previous article,[5] as $\Delta H = -19{,}250$ joules. The following calculation illustrates the method.

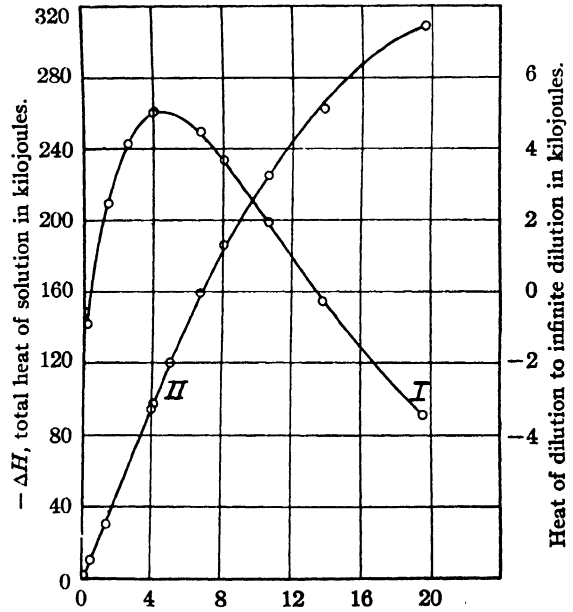

Fig. 1.—Curve I, heat of dilution to infinite dilution. Curve II, total heat of solution.

Let $x H_2O$ designate the amount of water required to form a 1.393 molal solution of $Ca(NO_3)_2$ containing one mole of $Ca(NO_3)_2$.

$$Ca(NO_3)_2(s) + yH_2O \longrightarrow Ca(NO_3)_2(aq.);\ \Delta H = -19{,}250\text{ j.}$$

$$Ca(NO_3)_2(1.393\ m) + (y - x)\ H_2O \longrightarrow Ca(NO_3)_2(aq.);\ \Delta H = +2479\text{ j.}$$

Subtracting $Ca(NO_3)_2(s) + xH_2O \longrightarrow Ca(NO_3)_2(1.393\ m);\ \Delta H = -21{,}729\text{ j.}$

This gives the change in heat content when a mole of solid calcium nitrate anhydride is dissolved in enough water to give the designated concentration. These heats of solution are tabulated in Column 8, Table I. These heats multiplied by the values of the concentrations, *m*, in column 2, give the heats of solution of *m* moles of calcium nitrate anhydride in 1000 g. of water, as tabulated in Column 9. The total heats of solution in Column 9 were plotted against the concentrations in Column 2, giving Curve II in Fig. 1. The slope of this curve, $d(\Delta H)/dm$, gives the partial molal heat of solution of calcium nitrate, ΔH_2, at the designated concentrations. This slope was obtained by setting up equations for the curve and differentiating with respect to *m*. The circles represent the values given in Column 9. The solid line represents the graph of the equations.

Values for the partial molal heats of solution of calcium nitrate, $d(\Delta H)/dm = \Delta H_2$, are tabulated in Column 3, Table II. Column 1 contains the molal concentration and Column 2 the mole ratio in the various solutions. These partial molal heats of solution are plotted against concentration in Curve I, Fig. 2. The *y* intercept, −20,599 joules, was calculated at zero concentration from the equation for the total heat of solution.

TABLE II

PARTIAL MOLAL HEATS OF SOLUTION OF $Ca(NO_3)_2$ AND OF H_2O

Concentration			ΔH_1		
m 1	n_2/n_1 2	ΔH_2, j. 3	From heat measurements, j. 4	From v. p. measurements, j. 5	Deviation (5) − (4), j. 6
1.542	0.0278	−24,100	+ 50	+ 150	+100
2.687	.0484	−25,100	+ 60	+ 320	+260
6.021	.1085	−22,250	− 150	− 30	+120
8.805	.1586	−17,600	− 750	− 880	−130
12.150	.2189	−13,150	−1590	−2070	−480
15.826	.2852	− 8,500	−2780	−2750	+ 30
17.53	.3157	− 6,350	−3420	−3430	− 10
19.62	.3534	− 3,700	−4300	−4790	−490
20.29	.3655	− 2,750	−4650	−4960	−310
20.87	.3760	− 2,000	−4920	−5300	−380

Partial molal heats of solution of water, ΔH_1, were calculated from the total heats of solution and the partial heats of solution of calcium nitrate by means of equation (1). Curve II, Fig. 2, is the partial molal heat of solution of water determined in this manner; the values are tabulated in Table II, Column 4.

Partial heats of solution of water from vapor pressure data can be calculated by means of thermodynamic equations. The process of dissolving one mole of water in a large body of solution without change in concentration can be considered to take place in three isothermal steps. One mole of water vapor is evaporated at its own vapor pressure. This vapor is then expanded from the vapor pressure of water to the vapor pressure of the solution. It is then condensed into an infinite quantity of solution. The heat involved in this process, ΔH_1, is the sum of the individual heat changes in the three steps. If water vapor is assumed to be a perfect gas at these low pressures, the heat involved in step 2 becomes negligible. Applying the Clapeyron–Clausius equation, with the usual assumptions, to the first and third steps gives the equation

$$\Delta H_1 = (RT_2T_1/(T_2 - T_1)) \ln (p_2p_1'/p_1p_2') \qquad (2)$$

where p_1 and p_2 are the vapor pressures of water at temperatures T_1 and T_2 and p_1' and p'_2 are the corresponding properties for the solution. Equation (2) is essentially the Kirchhoff[6] equation. Porter[7] derived and discussed Kirchhoff's equation from a standpoint of change in internal energy and pointed out that the steps indicated above are applicable to changes in heat content.

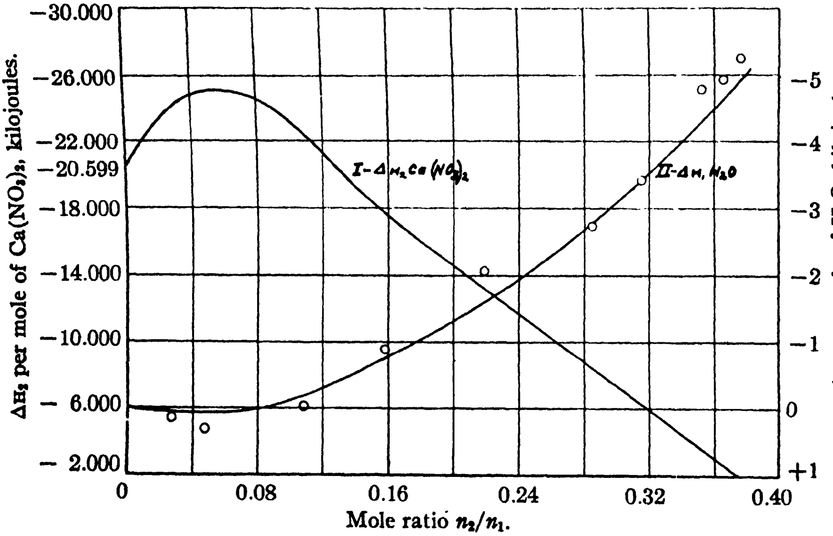

Fig. 2.—Partial molal heats of solution of $Ca(NO_3)_2$ and of H_2O.

Values of ΔH_1 calculated from equation (2) using the vapor pressures of calcium nitrate solutions measured by Ewing[8] are tabulated in Table II, Column 5. Values of ln p were plotted against $1/T$ and pressures were picked from the resulting straight lines at 20 and 30°. These calculated values of ΔH_1 are indicated as circles on Curve II, Fig. 2. The deviations of the values of ΔH_1 calculated from heat measurements and from vapor pressure measurements are tabulated in Column 6, Table II. The average deviation of 230 joules represents a deviation of 0.1 mm. in the vapor pressure of the 1.4 m solution and 0.003 mm. for the 19 m solution. The author estimated a maximum error of 0.1 mm. in the vapor pressure measurements.

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(6) Kirchhoff, *Ann. Physik Chem.*, [2] 103, 200 (1858).

(7) Porter, *Trans. Faraday Soc.*, 11, 19 (1915).

(8) Ewing, THIS JOURNAL, 49, 1963 (1927).

The authors wish to acknowledge their indebtedness to Mr. R. J. DeGray for assistance with the electrical hook-up and to Mr. Simon Deptula for translating Russian literature on heats of dilution.

Summary

1. Heats of dilution of calcium nitrate solutions to infinite dilution have been measured. The concentrations of the solutions studied range from 1.39 *m* to 19.55 *m*.

2. The total heat of solution of calcium nitrate and the partial heats of solution of calcium nitrate and of water have been evaluated by means of the heat of dilution measurements.

3. Values of the partial heat of solution of water calculated from calorimetric measurements have been compared with those calculated by means of Kirchhoff's equation from vapor pressure measurements.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. VIII. Conductance of Some Ternary Salts in Liquid Ammonia

BY CHARLES A. KRAUS AND PAUL B. BIEN[1]

I. Introduction

In the three preceding papers of this series,[2] results have been presented for the conductance of various types of binary salts in liquid ammonia with a view to determining the influence of ion constitution on the properties of electrolytes, particularly the dissociation constant. It seemed of interest to extend the investigation to ternary salts. Little is known regarding the behavior of ternary salts in non-aqueous solvents, particularly of ternary salts of divalent negative ions. Usually, ternary salts are very difficultly soluble in liquid ammonia although there are a few salts, most of them of somewhat complex structure, which are readily soluble.

When benzophenone is treated with two atomic equivalents of sodium, the well-known disodium ketyl salt is formed. With one equivalent of sodium,[3] a monosodium salt is formed which may be looked upon either as a binary salt derived from the anion $(C_6H_5)_2CO^-$ or as a disodium salt of the divalent benzpinacol ion. It was hoped that conductance measurements might throw some light on this question. The dialkyl and diaryl tin derivatives, when treated with two atomic equivalents of sodium, yield compounds of the type Na_2SnR_2,[4] which are readily soluble in liquid ammonia and in which, presumably, there exists the divalent ion, $R_2Sn^{=}$. These salts are of particular interest because both charges are associated with the same atom, in place of two different atoms as is the case in the derivative of benzophenone. Unfortunately, disodium diphenylstannide undergoes reaction (presumably with the solvent) at concentrations below about 200 liters. It was found possible, however, to form a salt, $Na_2[Sn(C_6H_5)_2]_2$, which may be looked upon as the disodium salt of tetraphenyldistannane. Here again it is possible that the Sn–Sn bond breaks down in solution to yield the univalent ion R_2Sn^-. It was thought that conductance measurements might throw some light on the state of the electrolyte in solution. A similar type of salt is obtained on treating hydrazobenzene with sodium or potassium amide. Here, we have a salt corresponding to the formula $M_2[N(C_6H_5)]_2$ which may dissociate to give the simple ion $C_6H_5N^-$. It might be expected that, upon treating this salt with additional sodium, disodiumphenylamide, $Na_2NC_6H_5$, might be formed. However, no reaction occurs when disodium benzhydrazide is treated with additional atoms of sodium. For purposes of comparison with monosodium diphenylketyl, the conductance of sodium benzhydrolate was measured.

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[1] Metcalf Fellow in Chemistry at Brown University.

[2] Kraus and Hawes, THIS JOURNAL, 55, 2776 (1933); Kraus and Kahler, *ibid.*, 55, 3537 (1933); Kraus and Johnson, *ibid.*, 55, 3542 (1933).

[3] Wooster, *ibid.*, 50, 1388 (1928).

II. Apparatus and Procedure

The apparatus employed in the present investigation was substantially the same as that of Kraus and Hawes and need not be described here. Some minor changes were introduced, the most important of which was that the solution was stirred by boiling. A platinum tube, closed at the bottom, was sealed into the tube connecting the two chambers of the cell at the bottom (see Kraus and Hawes). A small heater was constructed consisting of a copper rod, the end of which projected into the platinum tube and the upper part of which was wound with resistance wire which was electrically insulated from the copper rod. Heat was transmitted from the copper rod through the platinum tube into the solution, which was thus boiled and stirred very conveniently. Three-way stopcocks were attached to the withdrawal tubes used for emptying the cell or for withdrawing solution. These stopcocks eliminated one additional stopcock in each case and permitted connecting the top of the capillaries with the interior of the cell when the process of withdrawal was completed.

The method of making up the solution and of carrying out the dilutions was the same as that of Kraus and Hawes. The cell was calibrated against a standardized reference cell and the electrical measuring apparatus was the same as that used in previous work. Before making up the solutions, the cell was washed until the conductance reached a value of approximately 1×10^{-7}. No corrections have been applied to the data for the conductance of the solvent. Monosodium and disodium diphenylketyl were made up by treating benzophenone with one and two atoms of metallic sodium. The monosodium ketyl was also prepared by treating benzpinacol with sodium amide. The conductance values were the same for the two methods of preparation.

Sodium benzhydrolate was prepared by treating benzhydrol with sodium amide. It might be expected that disodium diphenylketyl might be prepared by treating benzhydrol with two equivalents of sodium amide. This, however, was not the case. In liquid ammonia solution, neither sodium nor potassium amide acts upon the monoso-

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(4) Kraus and Greer, THIS JOURNAL, 47, 2568 (1925); Kraus and Brown, *ibid.*, 52, 4031 (1930).

dium or potassium salt of benzhydrol. The solutions were in all cases colorless and the conductance corresponded to that of a mixture of the amide and the mono-salt of benzhydrol. When the solvent was evaporated and the mixture of benzhydrolate and amide heated to room, or higher, temperatures, reaction occurred as was indicated by the appearance of the red color characteristic of the dimetal ketyl. There is here an interesting case where a salt is stable in liquid ammonia solution without hydrolysis but which cannot be made by the action of a base on the corresponding acid.

Disodium benzhydrazide was prepared by the action of sodium amide on hydrazobenzene. Monosodium hydrazobenzene could not be prepared. If hydrazobenzene is treated with one equivalent of sodium amide, the disodium salt is formed and the additional hydrazobenzene is not acted upon. It was found impossible to split the N–N bond to form disodium phenylamide by treating disodium benzhydrazide with an equivalent amount of sodium. Neither was it possible to prepare the salt by the action of sodium amide upon monosodium phenylamide. An attempt to carry out measurements with the disodium salts of dihydroxybenzenes was unsuccessful because of the fact that none of these salts was appreciably soluble in liquid ammonia.

III. Results

Equivalent conductance values of the various salts are given in the following table. Although in a number of instances the conductance was measured below 10^{-4} *N*, the data are not presented since it was felt that they were not sufficiently reliable. The conductance of the solvent introduces uncertainties at lower concentrations, particularly in the case of salts that are poor conductors.

TABLE I

CONDUCTANCES OF SALTS IN LIQUID AMMONIA AT −33°

Disodium Tetraphenyldistannide, $Na_2[Sn(C_6H_5)_3]_2$

V	Λ	V	Λ
79.17	82.79	1307	137.6
140.1	91.56	2274	156.2
245.2	101.2	3956	178.2
429.2	111.6	6845	202.6
746.7	122.7	...	...

Monosodium ketyl, $NaOC(C_6H_5)_2$

V	Λ	V	Λ
44.08	31.43	801.1	71.77
66.81	34.78	1204	81.90
101.4	38.96	1790	92.30
153.8	43.71	2663	103.6
233.1	49.14	4040	116.0
353.8	55.60	6010	131.1
528.6	62.82	9058	147.0

Dipotassium Diphenylhydrazide, $K_2(NC_6H_5)_2$

V	Λ	V	Λ
27.50	13.37	560.4	41.44
42.63	15.83	930.3	49.56
71.62	19.15	1544	59.01
119.6	23.36	2563	68.43
199.8	28.42	4230	79.43
331.6	34.32	...	...

Sodium Benzhydrolate, $NaOCH(C_6H_5)_2$

V	Λ	V	Λ
95.40	13.09	1029	41.14
143.1	14.41	1718	51.52
217.0	18.28	2870	65.23
364.6	24.29	4763	82.97
616.2	32.11	7953	106.7

Disodium ketyl, $Na_2OC(C_6H_5)_2$

V	Λ	V	Λ
17.87	15.68	478.9	50.00
26.80	17.04	852.5	61.90
47.95	20.87	1517	75.45
83.95	26.26	2670	95.70
150.3	33.39	4673	120.0
269.0	40.98	8270	148.7

Only one series of measurements is given for each salt, although check determinations were made in the case of all salts with the exception of dipotassium diphenylhydrazide.

IV. Discussion

The conductance curves are shown graphically in the accompanying figure, where the logarithms of concentrations are plotted as abscissas and the conductance values as ordinates. Inspection of the figure will show that practically all the salts are rather weak electrolytes. For purposes of comparison, there are drawn curves for sodium triphenylstannide ($K = 130 \times 10^{-4}$) and sodium phenolate ($K = 3.82 \times 10^{-4}$). It will be noted that, although sodium phenolate is quite a weak electrolyte in liquid ammonia, it is a better conductor than most of the salts measured in the present investigation. The conductance curve for sodium phenolate rises much more steeply than does that of the salts which we have measured.

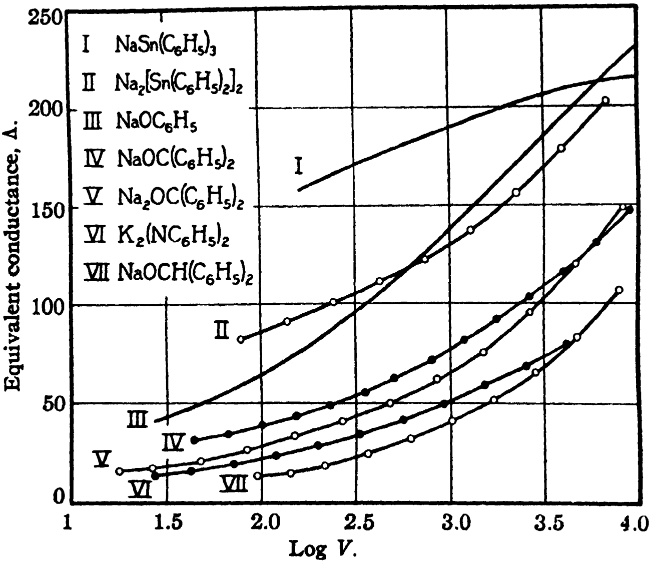

Fig. 1.—Conductance of salts in liquid ammonia.

According to the Debye–Hückel theory, we should expect the conductance of ternary salts to be much lower than that of corresponding binary salts. If a mass action effect occurs, as in the case of binary electrolytes, the constitution of the ions should have a marked influence on conductance.

The conductance curve for disodium ketyl lies slightly below that of the monosodium salt at higher concentrations but very nearly coincides with it at low concentrations. This indicates that the ionization of the two salts is approximately the same. Analysis of the curve for monosodium ketyl according to the method of Fuoss and Kraus[5] indicates that we are not dealing here with a simple binary equilibrium. It is impossible, however, to state definitely that the equilibrium is a purely ternary one. It is possible that a combination of binary and ternary equilibria exists and it is also conceivable that the charge on the monoketyl ion oscillates between oxygen and carbon. It is a remarkable fact that monosodium ketyl is a much better conductor than sodium benzhydrolate. The only difference between the two salts is that a hydrogen atom is associated with the aliphatic carbon atom in the one case and not in the other. It seems evident that constitutional factors play a large part in the dissociation phenomenon in the case of these salts.

Disodium benzhydrazide is a much weaker electrolyte than disodium ketyl. The low conductance value of this electrolyte indicates that we are here dealing with a ternary equilibrium. If the N–N bond were broken, the conductance of the resulting binary electrolyte should correspond approximately to that of sodium or potassium phenylamide. The conductance of potassium phenylamide has been measured by Kraus and Hawes and is enormously greater than that of the benzhydrazide here measured.

Disodium tetraphenyldistannide is a relatively good electrolyte. At low concentrations the conductance approximates that of sodium triphenylstannide but at higher concentrations the conductance is much below that of the binary salt, as may be seen from the figure. Evidently, we have to deal, here, with a ternary salt, but there is a possibility that an equilibrium exists between the univalent ions $(C_6H_5)_2Sn^-$ and the divalent ion $[(C_6H_5)_2Sn]_2^{=}$. It is known that the Sn–Sn bond is weak and it is quite conceivable that it is broken down under the action of electrostatic repulsion.

Although the data admit of only a qualitative interpretation, they seem to show that the ternary salts of divalent negative ions are much less highly ionized than are corresponding binary salts, and that, as in the case of salts of simpler ions, the dissociation as indicated by the conductance is the greater the larger the negative ion. It is hoped that at a later date more exact data may be presented. For this purpose, the experimental technique is being perfected.

Summary

Conductance values are presented for a number of salts of ternary type in liquid ammonia. In several of these salts the charges on the anion are associated with different atoms and there exists the possibility of dissociation of the anion complex into simple ions.

The results are discussed. Dipotassium diphenylhydrazide seems to behave like a ternary salt. In the case of disodium tetraphenyldistannide, there is evidence of dissociation of the anion complex. The conductance

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(5) Fuoss and Kraus, THIS JOURNAL, 55, 470 (1933).

curve for monosodium diphenylketyl does not correspond to that of a simple binary electrolyte.

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Properties of Electrolytic Solutions. IX. Conductance of Some Salts in Benzene

BY RAYMOND M. FUOSS AND CHARLES A. KRAUS

I. Introduction

In the first paper of this series,[1] the conductances of tetraisoamylammonium thiocyanate and of tri-isoamylammonium picrate in benzene were reported. With the apparatus then available, it was impossible to investigate the conductance at concentrations below the minimum; in fact, it was only possible to argue by inference from the behavior in mixed solvents that the conductance in a strictly non-polar solvent such as benzene would show a minimum. The appearance of inflection points in the conductance curves in the neighborhood of 0.001 N for some salts and not for others also made further experimental work desirable. It seemed especially important to determine, experimentally at least, how the complexity of the curve depended upon the ions of the electrolyte.

By constructing cells with constants as low as 0.003 and by improving the electrical measuring system, it has been possible to measure conductances at concentrations below 10^{-6} N with an accuracy of several per cent. We report herewith the conductance of tetraisoamylammonium thiocyanate, picrate, iodide, bromide, chloride and fluoride in benzene at 25°. Actual minima in conductance, followed by slopes approximating that required by the law of mass action, were found in the case of the picrate, thiocyanate, iodide and bromide; and the minimum was located for the chloride and fluoride. Dissociation constants calculated from the conductance data are of the order of 10^{-18}; among the halides, the iodide is the strongest salt ($K = 5 \times 10^{-18}$) and the fluoride is the weakest ($K = 6 \times 10^{-19}$), which is the order one might expect in non-polar (not solvating) solvents.

II. Materials, Apparatus and Method

Salts.—The preparation of tetraisoamylammonium thiocyanate and iodide has already been described. The iodide used as the starting material for this series of experiments melted at 141°, which is 5° higher than our previous value. The picrate, bromide, chloride and fluoride were prepared by neutralizing the hydroxide with the corresponding acid in alcoholic solution. The picrate was recrystallized from alcohol; the other salts were used directly as obtained from (room temperature) evaporation of the solution in which they were prepared. The fluoride is *extremely* hygroscopic; for the conductance experiments, samples were placed in a small weighing bottle which was heated to constant weight *in vacuo* at 70°. Dry air was admitted to the vacuum oven before capping the weighing bottle, which, after weighing, was emptied into a conductance cell previously evacuated and filled with dry air.

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[1] Kraus and Fuoss, THIS JOURNAL, 55, 21 (1933).

Benzene.—In addition to the treatment previously described, the benzene for these experiments was refluxed for six hours over (molten) potassium.

Conductance Cells.—For concentrations greater than 10^{-4} *N*, cells of several designs were used, much like those previously described. For the most dilute solutions, a different model was constructed (Fig. 1). The electrodes are three platinum cylinders, 5 cm. long and 8, 10 and 12 mm. in diameter, held concentrically by means of lead glass beads fused around light platinum wires welded to the cylinders. The seams are soldered with gold. The inner and outer cylinders are connected by platinum wires, so that both surfaces of the central cylinder are used. The lead wires from the cylinders are connected to thin platinum tubes which are sealed through the Pyrex glass envelope[2] at one end as shown in the figure, the exterior copper leads being soldered to the ends of the platinum tubes. The cell constant was found to be 0.003049 by indirect comparison with a cell standardized by means of 0.1 demal potassium chloride solution. The volume of the electrode compartment is about 17 cc.

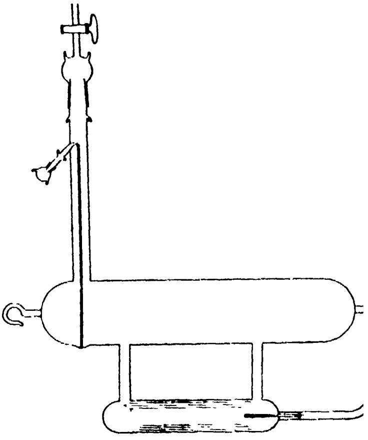

Fig. 1.—Conductance cell.

Manipulation was as follows: benzene was pumped by dry air pressure from a 250-cc. storage cell (into which it was distilled immediately before the conductance experiment) onto a sample of salt weighed into the cell. After weighing the cell, and determining the conductance, the cell was wiped free from thermostat oil and weighed. Then, by means of dry air pressure applied through the stopcock in the cap, about half of the solution was blown out through the sealed-in capillary siphon. The cell was weighed, and a portion of pure benzene was pumped in. The dilution ratio could be varied from 0.3 to 0.6, depending on the relative amounts of solution emptied and benzene added.

Electrical Equipment.—The previous method of using a sensitive galvanometer as ammeter has been discarded in favor of a Wheatstone bridge circuit. The cell formed one arm of the bridge, a megohm wire-wound coil[3] the second, a 0–10,000 ohm dial resistance box the third, and either a 10^4, 10^5 or 10^6 ohm coil the fourth. The bridge current was furnished by three 45-volt radio B-batteries and balance was determined by means of a galvanometer whose sensitivity was 10^{-10} amp./cm. at 2 meters scale distance. Corrections for solvent conductance, and for conductance of the glass between the electrodes and other leaks amounted to about 3×10^{-15} mho.

III. Experimental Results

The experimental results are given in Tables I–VI, and are shown graphically in Fig. 2. It will be noted that the conductances in the dilute region for the thiocyanate are somewhat higher than those previously

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(2) C. A. Kraus, Conducting-Seal for Vacuum-Containers, U. S. Patent 1,093,997, patented April 21, 1914.

(3) Shallcross Manufacturing Company, Collingdale, Pa.

reported. The measurements were extended to concentrations as low as 10^{-7} N, but, with the present methods, were somewhat erratic at concentrations below 10^{-6} N. The low concentration conductances, in general, appeared to be too high, perhaps due to traces of moisture. We intend to investigate the low concentration region in solvents of low dielectric constant in a closed system where even slight contamination can be

TABLE I

TETRAISOAMYLAMMONIUM PICRATE IN BENZENE AT 25°

$c \times 10^3$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^5$	$\Lambda \times 10^4$	$c \times 10^6$	$\Lambda \times 10^4$
13.20	108.1	9.25	3.26	15.07	1.11	14.80	1.07
9.31	60.5	6.86	2.46	11.93	1.02	14.66	1.02
6.79	36.24	6.75	2.53	10.53	1.00	14.32	1.12
4.57	20.01	4.77	1.88	8.30	0.96	9.41	1.22
3.34	12.92	4.53	1.87	6.27	.92	8.43	1.18
3.29	13.09	3.10	1.54	5.64	.92	4.33	1.65
2.405	8.47	3.07	1.45	3.85	.91	2.31	2.14
2.265	8.18	2.27	1.31	3.72	.91	1.20	3.04
1.488	5.06	2.17	1.28	2.54	.94	0.66	4.5
1.025	3.52	1.94	1.19	2.20	.94	..	..

TABLE II

TETRAISOAMYLAMMONIUM THIOCYANATE IN BENZENE AT 25°

$c \times 10^6$	$\Lambda \times 10^4$
102.2	2.43
41.9	1.26
14.32	1.02
6.55	1.43
2.808	2.29
1.152	4.0

TABLE III

TETRAISOAMYLAMMONIUM IODIDE IN BENZENE AT 25°

$c \times 10^5$	$\Lambda \times 10^4$	$c \times 10^6$	$\Lambda \times 10^4$
11.88	3.32	13.40	1.28
5.34	2.25	8.45	1.27
3.44	1.78	5.91	1.55
3.21	1.69	4.87	1.54
2.075	1.38	3.09	2.03
1.682	1.40	1.68	3.17

TABLE IV

TETRAISOAMYLAMMONIUM BROMIDE IN BENZENE AT 25°

$c \times 10^3$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^5$	$\Lambda \times 10^4$	$c \times 10^6$	$\Lambda \times 10^4$
34.22	58.0	29.74	3.86	16.85	2.60	18.73	0.96
22.25	20.7	20.35	3.58	9.86	2.07	15.38	.94
15.02	10.49	12.77	3.48	8.59	1.84	6.34	1.18
9.97	6.74	7.29	3.32	5.79	1.51	2.29	1.85
6.81	5.18	4.56	3.17	3.83	1.14	0.98	3.1
4.58	4.32	3.11	3.03	3.61	1.15	..	..

TABLE V

TETRAISOAMYLAMMONIUM CHLORIDE IN BENZENE AT 25°

$c \times 10^3$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^5$	$\Lambda \times 10^4$
33.02	42.0	33.98	3.82	14.71	1.69
23.17	18.40	23.09	3.47	9.68	1.26
15.57	9.45	15.51	3.22	6.65	1.07
10.72	6.40	5.97	2.90	3.87	0.68
7.21	4.83	3.67	2.50	2.01	.56
4.80	3.99	2.20	2.10	..	..

TABLE VI

TETRAISOAMYLAMMONIUM FLUORIDE IN BENZENE AT 25°

$c \times 10^3$	$\Lambda \times 10^4$	$c \times 10^4$	$\Lambda \times 10^4$	$c \times 10^5$	$\Lambda \times 10^4$
28.15	22.49	25.61	4.26	20.33	1.03
18.88	12.26	16.83	3.74	13.78	0.72
13.00	8.55	11.46	3.29	9.01	.52
8.88	6.57	8.41	2.92	5.61	.39
5.91	5.36	5.85	2.44	3.18	.32
3.88	4.60	4.35	2.02	1.58	.32
..	..	2.97	1.47	..	..

avoided. In the present communication, therefore, no data are given for the extremely dilute range. No attempt was made to carry the conductances to very high concentrations. It might be mentioned, however, that all of the halides appear to be quite soluble except the iodide, whose saturation concentration at 25° is less than 10^{-3} N. The picrate liquefies on the addition of a small amount of benzene, but the liquid phase produced requires a considerable volume of benzene for complete solution. Saturation is less than 0.1 N.

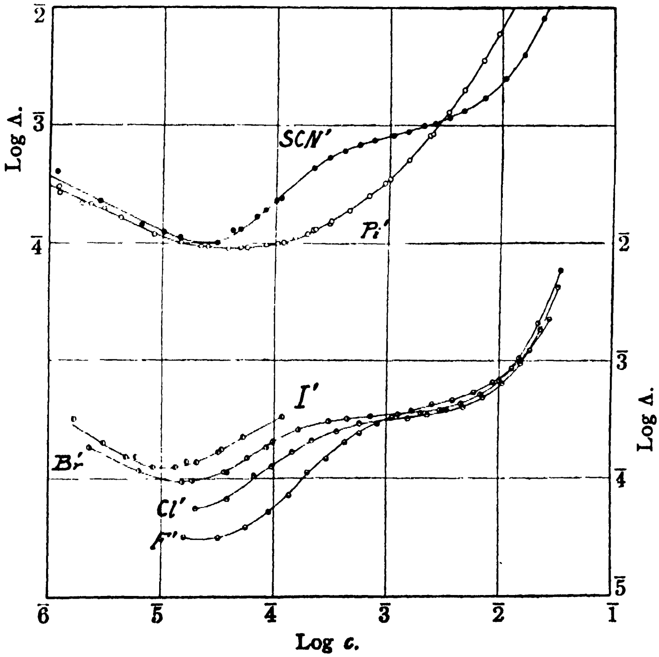

Fig. 2.—Conductance curves for tetraisoamylammonium salts in benzene at 25°.

IV. Discussion

As may be seen from Fig. 2, all the salts exhibit a conductance minimum at concentrations between 10^{-4} and 10^{-5} N, and in those cases (picrate, thiocyanate, iodide, bromide) where the specific conductance was sufficiently large to permit measurement at low concentrations, the rise in conductance below the minimum is in agreement with the slope of -0.5 required by the law of mass action. We conclude, therefore, that electrolytes exhibit a normal behavior in non-polar solvents.

At concentrations above 0.01 N, the equivalent conductance in all cases shows the very rapid increase with concentration which is characteristic of electrolytic solutions in solvents of low dielectric constant. Between the minimum and the higher concentration range is the region where inflection points may occur in the conductance curve. Their appearance seems to depend very much on the nature of the electrolyte: they are very noticeable for the bromide and are entirely lacking for the picrate. In the case of the halides, it is only in the neighborhood of the first inflection after the minimum that the curves show any marked differences from each other. Evidently, this region is controlled primarily by the specific properties of the ions involved. Two of these have been identified, namely: the distance parameters a and a_3 which, together with the dielectric constant and the temperature, are sufficient to describe the binary equilibrium $A^+ + B' \rightleftharpoons AB$ and the triple ion equilibrium $AB_2' + A_2B^+ \rightleftharpoons 3AB$.

By means of equation (8) of our previous paper,(4) it is possible to calculate $K\Lambda_0^2$ from the data locating the minimum in conductance. Although values of the limiting conductance Λ_0 are not known for electrolytes in benzene, a good estimate of the order of magnitude of the mass action constant K can be made by setting $\Lambda_0 = 100$ for all the salts. This value is based on the viscosity of benzene,(5) $\eta_{25} = 0.0060$, and a round value of Walden's constant for the product $\Lambda_0\eta$ for salts of the type studied here. This estimate for Λ_0 can hardly be in error by more than ±50%, which corresponds to only ±0.4 in log K. The results of this calculation are given in the third column of Table VII, which also includes, for the sake of comparison, values for the ternary isoamyl picrate.(6)

TABLE VII

CONSTANTS FOR SALTS IN BENZENE AT 25°

Salt	$-\log K\Lambda_0^2$	$-\log K$	$-\log k$
$(C_5H_{11})_4NOC_6H_2(NO_2)_3$	13.05	17.05	4.85
$(C_5H_{11})_4NSCN$	13.25	17.25	5.15
$(C_5H_{11})_4NI$	13.30	17.30	5.40
$(C_5H_{11})_4NBr$	13.45	17.45	5.30
$(C_5H_{11})_4NCl$	13.90	17.90	5.20
$(C_5H_{11})_4NF$	14.20	18.20	5.10
$(C_5H_{11})_3HNOC_6H_2(NO_2)_3$	16.60	20.60	3.40

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(4) Fuoss and Kraus, THIS JOURNAL, 55, 2390 (1933).

(5) Landolt–Börnstein, Tables, p. 145.

(6) Kraus and Fuoss, THIS JOURNAL, 55, 21 (1933).

The quaternary picrate is the strongest salt of the group and the ternary picrate is much the weakest. Particularly interesting is the series presented by the four halides: $K\,(\mathrm{I}') > K(\mathrm{Br}') > K(\mathrm{Cl}') > K(\mathrm{F}')$. In a nonpolar solvent we might expect complete absence of solvation (in the sense of orientation of solvent dipoles in the fields of the ions). In this event the halides should show a regular decrease in apparent ion size from iodide to fluoride, and the latter should be the weakest salt among the halides. This is precisely what we find experimentally. The decrease of K with decreasing atomic number is, in fact, probably greater than that calculated above, because the value of the *product* $K\Lambda_0^2$ *decreases* from iodide to fluoride, while the limiting conductance presumably increases.

The values of the parameter a calculated from the above constants and equations (5) and (6) of our third paper[7] range from 5.75×10^{-8} cm. for the quaternary picrate to 4.8×10^{-8} cm. for the ternary picrate.

The shift of the minimum with changing salt constitution is described by the constant k, given in the last column of Table VII. This constant[8] describes the equilibrium between free ions and ion pairs (dipoles), on the one hand, and ion triples, on the other. A large value of k (*i. e.*, small negative logarithm) corresponds to a low probability for the formation of an ion triple. The constant increases with increasing dissymmetry, either in relative size or in location of charge, of the ions which make up the salt; k is smallest for the quaternary iodide and greatest for the ternary picrate. The halide ions may all be represented as charged spheres, and here k increases as the size of the negative ion decreases, the size of the (rather large) positive ion remaining the same. It is interesting to note that, while the iodide and thiocyanate have nearly the same K for the binary equilibrium, the k for the triple equilibrium is larger for the thiocyanate, as is shown by the appearance of the minimum at a higher concentration. In the negative ion of the quaternary picrate, the charge is located on one end of the negative ion, and this reduces the chances of formation of ion triples; correspondingly, among the quaternary salts measured, k is greatest for the picrate. In the ternary picrate both ions could best be represented by ellipsoids with charges at one end of the longest axis, rather than by spheres, and this marked dissymmetry leads to a very large k. If we represent all ions as spheres, and calculate parameters a_3 by means of equations (14) and (16) of our fourth paper[8] we obtain $a_3 = 7.4 \times 10^{-8}$ for the quaternary iodide and 14.8×10^{-8} for the ternary picrate.

The appearance of inflection points on the high concentration side of the minimum also appears to be directly related to the symmetry of the salt. In the neighborhood of 10^{-3} N, the conductance curve of the bromide is almost horizontal, and the slope of this inflection region increases to chloride and fluoride, so much so in the latter case, that the fluoride curve, which lies below the others at high and at low concentrations, cuts across the others twice in this region. The thiocyanate has nearly the same inflection slope as the fluoride and the picrate curve exhibits no inflection points whatsoever. Preliminary calculations indicate that the complete conductance function is of the form

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[7] Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

[8] Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

$$\Lambda = A_{-1}c^{-1/2} + A_1c^{1/2} - A_2c + A_3c^{3/2} - A_4c^2 + - \dots$$

where the even powers of the square root of concentration correspond to the formation of ion clusters containing an even number of ions. The formation of the latter corresponds to a decrease in conductance with increasing concentration, and, depending on the relative magnitudes of the coefficients A_n, the inflection points are more pronounced, the greater the negative coefficients. There is at least qualitative agreement between the apparent molecular weights determined from freezing point measurements[9] and the apparent association calculated from conductance data. It therefore seems likely that it will be possible to account generally for the properties of electrolytic solutions up to moderate concentrations on the basis of equilibria between simple ions and more complex structures formed from them due to the action of Coulomb forces.

Summary

1. Conductances are reported for tetraisoamylammonium picrate, thiocyanate, iodide, bromide, chloride and fluoride in benzene at 25° in the concentration range 0.02–0.000001 *N*.

2. It is shown that the conductance of electrolytes in a non-polar solvent conforms to the law of mass action at low concentrations.

3. Relationships between the structure of electrolytes and their conductance curves in solvents of low dielectric constant are discussed.

PROVIDENCE, RHODE ISLAND

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[9] R. A. Vingee, Thesis, Brown University, 1932; F. M. Batson, unpublished work in this Laboratory.

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, AT THE UNIVERSITY OF CALIFORNIA]

The Heat Capacities of Sodium Carbonate and Bicarbonate and Silver Carbonate at Low Temperatures[1]

BY C. TRAVIS ANDERSON[2]

The measurements described in this paper, which are a part of a series carried out in this Laboratory in a general program of determination of the thermal properties of important metallic carbonates, had a further incentive in the desire to compare the entropies so obtained with the corresponding figures from thermal decomposition. A discrepancy of several units still exists in the entropy of carbon dioxide as determined from equilibria, the third law, or spectroscopic data.

The method, apparatus and accuracy have been described in previous publications.[3] A new calorimeter with a gold wire resistance thermometer was constructed and used in the heat capacity determinations of the sodium bicarbonate. The heat capacity measurements with this new calorimeter are probably better than 1% at 55°K., as the gold wire resistance thermometer does not have the rapid diminishing resistance or the decrease of temperature coefficient that the copper wire resistance has at this low temperature. At higher temperatures the errors are probably substantially the same as with the copper wire resistance thermometer.

Materials

The sample of sodium carbonate used was Merck anhydrous C. P., and analysis showed the impurities to total less than 0.1%. A 91.4-g. sample was studied.

The sample of sodium bicarbonate was a product of Squibb. An analysis showed it to be better than 99.8% sodium bicarbonate, the impurities being about 0.1% each of water and sodium carbonate. No correction was made for these small impurities. The calorimeter was filled with 127.0 g.

The sample of silver carbonate was prepared in this Laboratory. Silver nitrate prepared from pure silver foil and C. P. nitric acid was recrystallized several times, dissolved in a large volume of water and a deficiency solution of sodium carbonate was added to precipitate the silver carbonate. Carbon dioxide was passed into the cold liquid for several hours in the dark, the liquid decanted and more water added. This was continued until no traces of sodium nitrate could be detected in the supernatant liquid. It was then filtered by suction, washed, dried over sulfuric acid and finally over phosphorus pentoxide. A conversion to metal indicated a purity of 99.96% silver carbonate.

Hydrogen was used as the conducting gas in the first series of measurements. It was found to have reacted with the silver carbonate. To remedy this difficulty helium was then used as the conducting gas, with 261.7 g. of silver carbonate.

The Specific Heats.—No previous low temperature measurements have been made on any of these carbonates. The results obtained in this

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant Physical Chemist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, Calif.

[3] Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930); **54**, 107 (1932).

Laboratory on the heat capacities of sodium carbonate, sodium bicarbonate and silver carbonate, expressed in gram calories (15°) per gram formula weight, are shown graphically in Fig. 1. The experimental determinations of heat capacities for these carbonates are given in Tables I, II and III,

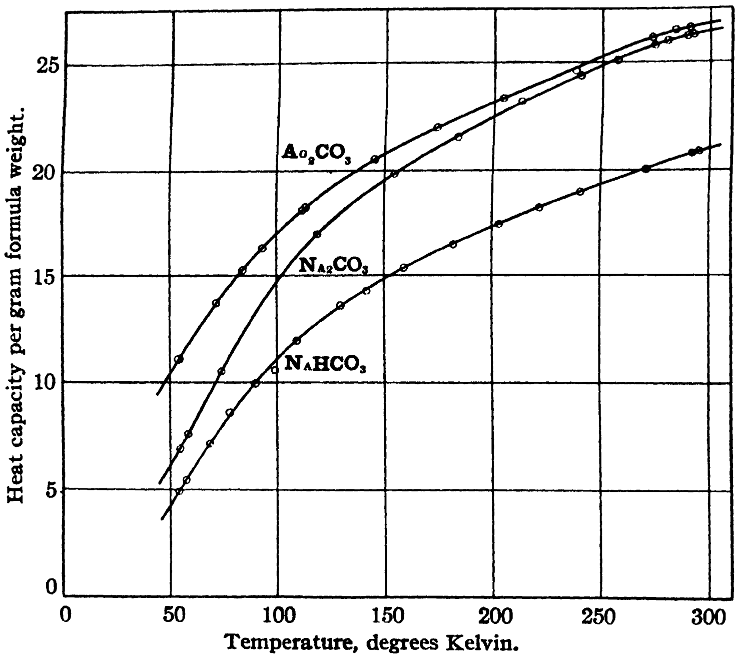

Fig. 1.—The heat capacities of sodium and silver carbonates and sodium bicarbonate, in calories per gram formula weights.

TABLE I

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF SODIUM CARBONATE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.60	6.878	154.6	19.88	256.7	25.12
58.43	7.579	183.6	21.56	292.1	26.29
74.23	10.53	212.6	23.24	274.1	25.81
119.2	16.96	239.7	24.43	280.2	26.01
				289.3	26.24

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF SODIUM BICARBONATE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.17	4.923	109.4	11.90	221.8	18.25
57.54	5.438	129.8	13.60	240.6	19.00
68.65	7.225	142.0	14.28	270.7	20.06
77.86	8.591	159.4	15.37	291.8	20.79
90.07	9.953	182.3	16.46	295.1	20.89
99.07	10.57	203.4	17.45		

TABLE III

HEAT CAPACITIES PER GRAM FORMULA WEIGHT OF SILVER CARBONATE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
53.51	11.06	93.57	16.28	204.2	23.39
54.46	11.10	112.0	18.12	237.4	24.65
71.57	13.71	113.7	18.25	272.9	26.16
84.25	15.26	145.2	20.52	283.7	26.50
93.53	16.28	173.9	22.03	290.4	26.62

respectively. In changing joules to calories the factor 1/4.184[4] was used. The calculations were made on the basis of Na = 22.997, C = 12.00, O = 16.00, H = 1.008, and Ag = 107.88.

Calculation of Entropies.—The entropies were calculated by the usual method of plotting the heat capacity against the logarithm of the temperature. The heat capacity curves were extrapolated to the absolute zero by means of combination of Debye and Einstein functions. The Debye functions used had the following parameters (Θ): for Na_2CO_3, 137.6; $NaHCO_3$, 209.5; and Ag_2CO_3, 96.2.

The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weights of these carbonates.

$$C_{Na_2CO_3} = D\,(138)/T + 2E\,(266)/T + 2D\,(737)/T$$
$$C_{NaHCO_3} = D\,(210)/T + 2E\,(292)/T + 2D\,(1601)/T$$
$$C_{Ag_2CO_3} = D\,(96)/T + 2E\,(172)/T + 2E\,(497)/T$$

The Na_2CO_3 combination fits the experimental heat capacity curve up to 200°K., the $NaHCO_3$ combination to 225° and the Ag_2CO_3 to about 160°. The results of the entropy calculations are given in Table IV.

TABLE IV

ENTROPY DATA

	Na_2CO_3	$NaHCO_3$	Ag_2CO_3
Extrap. (0–56.2) °K.	4.10	2.19	7.86
Graph. (56.2–298.1) °K.	28.40	22.20	32.13
S°_{298} graphical	32.5 ± 0.6	24.4 ± 0.4	40.0 ± 0.9
S°_{298} calcd. from functions	33.0	24.4	40.5

The related thermal data will not be mentioned at the present time, but will be fully discussed in a separate paper after the completion of this series of experiments.

Summary

The heat capacities of sodium carbonate, sodium bicarbonate and silver carbonate from about 55 to 300°K. have been determined and their corresponding entropies calculated as 32.5, 24.4 and 40.0, respectively.

BERKELEY, CALIFORNIA

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[4] "International Critical Tables," Vol. I, p. 24. 4.185 abs. joules = 1 cal. = 4.1837 Int. joules.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Ionization Constants of a Number of Methylated Quinolines and of Certain Saturated Bases Isolated from Petroleum Distillates

BY W. A. FELSING AND B. S. BIGGS

During an investigation dealing with extraction and identification of nitrogen bases[1] from petroleum distillates, it seemed worth while to determine the ionization constants of all the monomethylquinolines and of some of the higher homologs. All of the bases identified so far from petroleum distillates belong to the series just mentioned. It seemed desirable to ascertain any order, if such existed, in the variation of these constants with the location of the methyl radicals in the quinoline nucleus; it was also desirable to know the relative strengths of the aromatic and non-aromatic petroleum bases, since such information might be of value in devising a scheme of separating the two types of bases found in petroleum distillates.

The method adopted for this investigation was the electrometric determination of the $[H^+]$ produced by the hydrolysis of the perchlorates of the bases under consideration. Use was made of an accurate potentiometer set-up, a saturated calomel half-cell, and a platinum wire in conjunction with quinhydrone. The calomel electrode was standardized by measurement against a 0.05 *N* potassium acid phthalate buffer solution, the P_H of which was known. In the P_H determinations of the quinolines, the potentials were reproducible to 0.0002–0.0005 volt; a change of platinum electrodes did not alter the observed voltage. All determinations were made at 25 ± 0.05°. The method was based upon the hydrolytic reaction of the base perchlorates, $B^+ + HOH \rightleftharpoons BOH + H^+$. The relation, readily deduced theoretically, for the calculation of the ionization constants is

$$K_I \text{ of Base} = K_w \cdot [B^+]/[H^+]^2$$

where K_w is the ionization constant of water. If the assumption is made that the $[B^+] = C$, the total salt concentration (an assumption very nearly true if the salt of a highly ionized acid, such as perchloric, is employed), the relation becomes

$$K_I \text{ of Base} = K_w \cdot C/[H^+]^2$$

This latter relation was used to calculate the ionization constants listed in the table. All materials were repurified for this investigation; after conversion into perchlorates, the salts were further purified by recrystallization from water.

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[1] This investigation is a continuation of A. P. I. Project 20, under the general direction of Prof. J. R. Bailey. The work begun under this project is now being aided by the Union Oil Company, which is furnishing the nitrogen base concentrates.

THE IONIZATION CONSTANTS OF SOME RELATED NITROGEN BASES

Base	Source	(*E*)obs.	Calcd. *P*H	$K_I \times 10^9$
Quinoline	Eastman	0.2518	3.40	0.63
2-Methylquinoline	Synthetic[a]	.2336	3.71	2.64
3-Methylquinoline	Synthetic[a]	.2418	3.57	1.38
4-Methylquinoline	Eastman	.2405	3.60	1.59
5-Methylquinoline	Synthetic[a]	.2574	3.31	0.42
6-Methylquinoline	Synthetic[a]	.2482	3.46	.83
7-Methylquinoline	Synthetic[a]	.2437	3.54	1.20
8-Methylquinoline	Synthetic[a]	.2585	3.30	0.40
2,3-Dimethylquinoline	Petroleum[b]	.2479	3.47	.87
2,4-Dimethylquinoline	Petroleum[b]	.2426	3.56	1.32
2,6-Dimethylquinoline	Synthetic[a]	.2326	3.73	2.88
2,7-Dimethylquinoline	Synthetic[a]	.2458	3.51	1.04
2,8-Dimethylquinoline	Petroleum[b]	.2730	3.05	0.13
2,3,8-Trimethylquinoline	Petroleum[b]	.2630	3.21	.26
2,4,8-Trimethylquinoline	Petroleum[b]	.2617	3.24	.30
$C_{16}H_{25}N$ (a satd. base)	Petroleum[c]	.2417	3.57	1.38
$C_{13}H_{21}N$ (a satd. base)	Petroleum[c]	.2209	3.93	7.26

[a] Products synthesized and purified in this Laboratory. [b] Products extracted from petroleum distillates, purified and identified in this Laboratory. [c] Products extracted from petroleum, purified, but constitution yet to be determined.

The correlation between activity (as expressed by the ionization constant) and the location of the methyl radical is not striking. In the monomethylquinoline series, the location of the methyl radical on the nitrogen ring seems to have a larger influence upon the ionization constant than does location on the benzene ring, the decreasing order locations being 2, 4, 3. In this series, also, the 7-position of the benzene ring seems to produce the largest activity. The 2,6-position produces the greatest activity of the dimethylquinolines.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Adsorption of Gases on Palladium Oxide[1]

BY PAUL V. MCKINNEY

Palladium oxide is reduced readily at room temperature by hydrogen, reacting as rapidly as the gas comes into contact with it. However, the reduction proceeds slowly even at 100° when carbon monoxide is used[2] and is difficult to carry to completion short of 156°. This is unusual, for the heat of formation of water is less than the heat of formation of carbon dioxide from the monoxide, and the reduction of other oxides proceeds at a lower temperature with carbon monoxide.[2] Since adsorption of the gases is certainly one of the important steps in the rate of heterogeneous reactions, the adsorption of oxygen, carbon dioxide and carbon monoxide have been determined on palladium oxide and on partially reduced palladium oxide, *i. e.*, on an interface between the oxide and palladium. Adsorption on palladium itself has been previously investigated.[3] A series of less reducible oxides was studied by Benton,[4] who determined the adsorption of carbon monoxide only up to 0°, thus obtaining very little information concerning the relationship of adsorption to reduction.

Experimental

Preparation of Material.—The palladium oxide was prepared by the method of Shriner and Adams,[5] that is, from the chloride in fused sodium nitrate, washed and dried over phosphorus pentoxide. For the adsorption studies it was evacuated for three days at 256°, and washed twice with nitrogen. The sample weighed 47.0 g., equivalent to 40.8 g. of palladium or 0.383 mole. All gases were purified by the usual methods; volumes are given corrected to standard conditions.

Apparatus.—The apparatus is that described in another connection[6] and was constructed so that the adsorption could be followed either in a constant volume, or at constant pressure. In the present case the entire process was by the latter method at 350 mm. pressure. It was completely glass sealed, connecting directly with the gas purification train and with the collecting pumps and the system for analysis over mercury.

The adsorption vessel was surrounded by suitable constant temperature baths. The traps were cooled continually by a carbon dioxide–ether mush, to prevent the access to the active surface, of mercury vapor from the pumps and manometer as well as vapors from the stopcock grease. It was found necessary to keep this trap freshly packed with dry ice in order to maintain a constant temperature. The collecting pumps consisted of a Toepler pump and a Sprengel pump. The mercury vapor pump was placed in series just before the Sprengel pump and also connected to the oil pump. Thus removal of strongly adsorbed gas could be made at the speed and vacuum of the mercury vapor pump and yet the gas could be collected. The manometer was a constant vol-

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(1) Paper presented at the Washington Meeting of the American Chemical Society, March, 1933.

(2) McKinney, THIS JOURNAL, **54**, 4498 (1932).

(3) (a) Taylor and Burns, *ibid.*, **43**, 1273 (1921); (b) Taylor and McKinney, *ibid.*, **53**, 3604 (1931).

(4) Benton, *ibid.*, **45**, 887, 900 (1923).

(5) Shriner and Adams, *ibid.*, **46**, 1683 (1924).

(6) McKinney, *J. Phys. Chem.*, **37**, 381 (1933).

ume instrument with electrical contact; however, the current was not used in the measurement with oxygen. The change in adsorption was observed by the change in level of the confining mercury in the buret. With this apparatus an adsorption isobar may be plotted directly.

Method.—The inert volume of the system was determined with nitrogen. There is sufficient evidence that it is not adsorbed. It had been previously shown to be inert to a palladium surface and it seemed reasonable to expect it to be inactive toward the oxide. The nitrogen was all recovered in the collecting system and a plot of the volume of the system against the temperature gives a smooth curve. The values obtained in three measurements with nitrogen spaced before and during the adsorptions are in agreement. Temperature equilibrium was attained rapidly over the entire range, with complete reversibility. The values are identical with the amount of oxygen required to fill the apparatus. The dead space of the apparatus to the master stopcock was 25.9 cc. with the bulb at 0°.

After the determination with nitrogen the order of study was oxygen, carbon dioxide and carbon monoxide. In each case the gas was admitted to the highly evacuated oxide at a low temperature and the rate of adsorption observed. The temperature was then changed and the process continued. Following a series of higher temperature measurements, the system was again cooled and the process observed for comparison with earlier results. The temperature range was from −78 to 218° for the adsorptions, with evacuation at 256° to recover the last trace of gas. In addition to the study of the adsorption isobar in the case of carbon monoxide, the rate of adsorption was measured at definite temperatures on a completely evacuated sample with analysis of the gas at suitable time intervals. Following each isothermal measurement the gas was collected until completely recovered, and the system pumped out at 256° with the mercury vapor pump for two to four hours.

Results

Adsorption of Oxygen.—This gas was measured over the temperature range −78 to 218° with a divergence of ±0.3 cc. from the nitrogen values. It is concluded that this is the order of accuracy of the individual measurement and that oxygen is not adsorbed by a palladium oxide surface. At each temperature there was no drift of the oxygen volume with time over a period of two hours. Actually 45.7 cc. of oxygen was admitted and 45.3 cc. recovered with less than 0.5% not adsorbed by alkaline pyrogallol solution.

Five adsorptions of oxygen were attempted, the first before the palladium oxide had been reduced differed by 0.3 cc. from the nitrogen volume, the last after the oxide was 2% reduced agreed within 0.05 cc. This is contrary to the results of Taylor and Burns,[3a] who found oxygen to be as strongly adsorbed as carbon monoxide on free palladium. However, the palladium they used had been reduced by hydrogen and it is difficult to remove all the hydrogen except by sintering the metal. The small amount of water would not have been observed since it is also strongly adsorbed by palladium.

Finally the partially reduced sample was heated in oxygen at 218°, and though ten minutes' contact showed no adsorption at this temperature, 2.13 cc. was adsorbed in four hours, and exactly this amount could not be recovered by the pumps, having reacted chemically. Metallic palladium reacts with oxygen at about 830°.[7]

Adsorption of Carbon Dioxide.—This gas, which Taylor and Burns have shown is not adsorbed by palladium black, is adsorbed normally by palladium oxide, Fig. 1. The adsorption is greatest at low temperatures and gradually evaporates with temperature increase becoming negligible at 218°. The observations are for a pressure of 350 mm. On a partially reduced surface, *i. e.*, one having perhaps Pd atoms and Pd–PdO interfaces, the adsorption of carbon dioxide is less as is shown by the lower curves. It is however similar in nature. Actually the original 0.383 mole of palladium oxide has been reduced by 0.0021 mole of carbon monoxide, *i. e.*, by only 0.5% before the second adsorption of carbon dioxide. Since the dioxide is not adsorbed by palladium itself, the decrease may represent either a decrease in the total extent of palladium oxide surface by the reduction or that the active palladium oxide spots have been removed to that extent. Values for the adsorption of carbon dioxide obtained on reducing the temperature are marked in Fig. 1 with +. Since it attains temperature equilibrium rapidly and is completely reversible, the adsorption of carbon dioxide by palladium oxide is entirely physical adsorption.

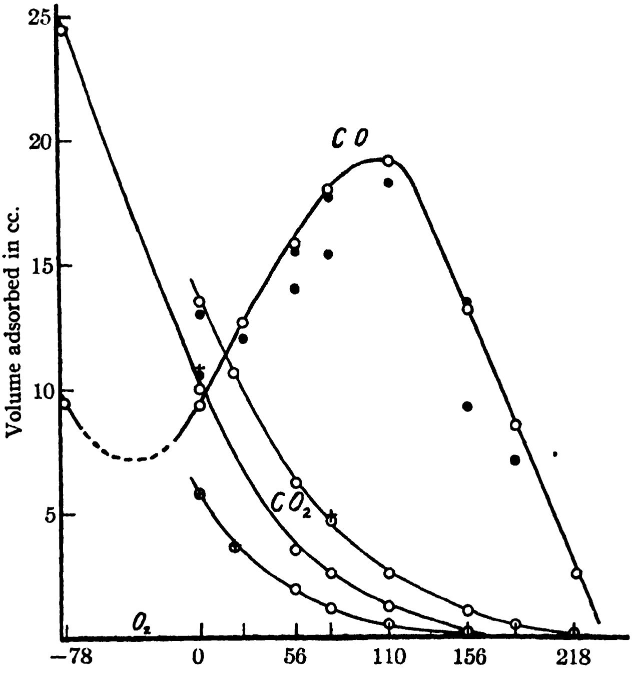

Fig. 1.—Adsorption on palladium oxide.

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[7] Lunde, *Z. anorg. allgem. Chem.*, **163**, 345 (1927).

Carbon Monoxide.—As we should expect the adsorption isobar with this gas is widely different. There is a moderate adsorption at low temperatures, increasing from room temperature to a maximum at about 110° and then decreasing. The values plotted are not equilibrium values as in the case of carbon dioxide but are those for an adsorption of thirty minutes at each temperature. If the process is continued longer there is a slight but significant change in the location of the points. At −78° the two values are identical, between that and the maximum the values for an adsorption at one hour all lie higher than for the thirty-minute periods. Beyond the maximum these points are lower.

Analysis of the gas removed by the pump following this isobar of carbon monoxide on palladium oxide gave 94% of carbon dioxide, the remainder being carbon monoxide. This is equivalent to 0.5% reduction of the entire sample of palladium oxide. When carbon monoxide was admitted to the partially reduced sample the adsorption was very similar to the previous case. However, the gas desorbed analyzed only 73% carbon dioxide. These measurements for thirty-minute adsorption at each temperature are plotted as dark circles in Fig. 1. A third set of values was obtained by the isothermal rate measurements of Fig. 3, and these are also plotted with the former. Analyses of the gas removed from the isothermal adsorption are collected in Table I.

TABLE I

ANALYSIS OF GAS REMOVED FROM CARBON MONOXIDE–PALLADIUM OXIDE SYSTEM

Volume in cc.; Time in hours; Carbon Dioxide Content in %

Method of removal		Toepler				Hg vapor pump		By heating
Temp. °C.		Time		Time		Time		
−78	Vol.	3.5	43.6					7.4
	CO$_2$		0					77
25	Vol.	4	32.04				3.3	10.8
	CO$_2$		0.5				37	82
56	Vol.	3	7.3	21	15.2		5.9	21.1
	CO$_2$		6		20		52	62
76	Vol.	3	4.3	15	24.4		10.5	9.6
	CO$_2$		2		18		19	75
156	Vol.	15 min.	2.8	2	3.6	5	30.2	6.2
	CO$_2$		1.8		13		61	78

The adsorption of carbon monoxide is not reversible. On cooling to 0 from 218° the amount of gas adsorbed greatly increased. If one assumes that on cooling the amount of carbon dioxide readsorbed will be equal to that adsorbed at 0° in the preceding experiment and that the amount of carbon monoxide readsorbed is that originally adsorbed in the present experiment then the total readsorbed gas may be calculated.

Readsorbed:	Expt. 4, 23.05 cc.;	Expt. 5, 19.00 cc.
CO$_2$	13.46	9.97
CO	9.30	10.44
Calculated readsorption	22.76	20.41

Discussion

Physical Adsorption.—The low temperature adsorption on palladium oxide is certainly of the physical type. At −78° there is no drift of the amount of gas adsorbed with time, Fig. 2, temperature equilibrium being established in about fifteen minutes. When the oxide has been partially reduced there is a slight drift in the adsorption at −78°. This is probably due to adsorption of carbon monoxide by the free palladium.[3b,8] The gas removed with the Toepler pump at −78° analyzed free from carbon dioxide; 7.4 cc. could not be removed even with the mercury vapor pump at this temperature. It seems reasonable to suppose that this represents carbon monoxide held by activated adsorption to palladium atoms. When this gas was removed at a higher temperature it analyzed 5.7 cc. of carbon dioxide and 1.7 cc. of carbon monoxide.

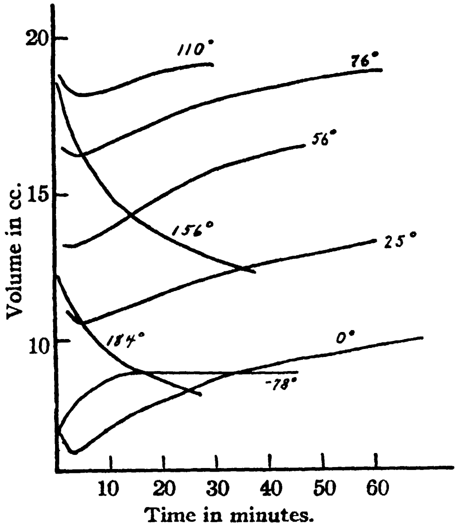

Fig. 2.—Rate of adsorption and desorption of carbon monoxide on palladium oxide.

Activated Adsorption and Reaction.—Between 0 and 100° the amount of carbon monoxide adsorbed increases with the temperature. Samples of the gas removed in this range showed varying amounts of carbon dioxide. On partial reduction the surface does not change much in extent and adsorption does not seem to penetrate the reduced material. However, certainly part of the adsorption in this case is on palladium. At 0° after each additional reduction the amount of adsorption increases, the dark circle lies higher, Fig. 1. At higher temperatures the values are not greater and in general less. This is reasonable since the maximum in the activated adsorption of carbon monoxide by palladium occurs at 0°, above which temperature the carbon monoxide rapidly evaporates from the free metal.

From the data of Fig. 3 activation energy of the process occurring in the rising portion of the curve of the adsorption of carbon monoxide may be calculated. The value of *E* for the volumes 8, 9 and 10 cc. between 0 and

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(8) On palladium the adsorption of carbon monoxide exhibited the same type of maximum. The low temperature process reached an equilibrium rapidly and reversibly. All the carbon monoxide was recovered. The activated or chemical process approached equilibrium more slowly. Above the maximum, the carbon monoxide may be completely recovered, but below this temperature it cannot be removed in any reasonable time even with the mercury vapor pump. We note that this activated adsorption begins on palladium around −78° and reaches a maximum about 0°.

25° is 2600 calories. Between 25 and 56° for 10 to 15 cc. adsorbed it varies from 3600 to 4800 calories. In the temperature range 56 to 76° the activation energy has again increased, ranging from 7800 calories for 10 cc. adsorbed to 10,000 calories for 15 cc. and 16,000 calories for 18 cc. adsorbed. The process occurring here must be complex since in the case of a simple activated adsorption the value of E should be constant. There is the adsorption of carbon monoxide on free palladium with its maximum below 25° which is decreasing in amount above this temperature although increasing in rate, as well as the adsorption of the monoxide on palladium oxide with a maximum above 76°. Reaction is occurring with some of the adsorbed molecules evaporating as carbon dioxide from palladium atoms, which introduces the heat of reaction into the observed value of E.

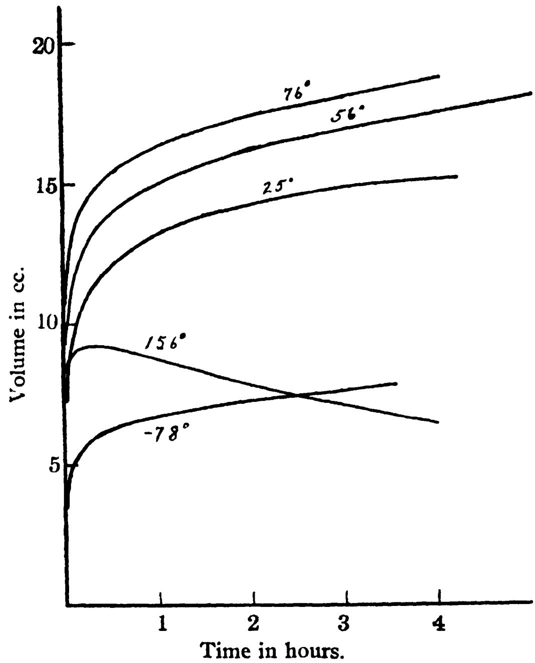

Fig. 3.—Rate of adsorption, carbon monoxide on palladium oxide.

Conclusion

The reduction of palladium oxide occurs through an adsorption step. However, unlike the case of most reducible oxides the process once begun is not autocatalytic and does not proceed to completion. The reduction in spite of the adsorption proceeds slowly. At −78° the carbon monoxide is adsorbed on palladium oxide physically and it may be recovered by evacuation. However, on a partially reduced sample even at this temperature the carbon monoxide is adsorbed strongly by the palladium atoms. Between room temperature and 110° the adsorption of carbon monoxide is chemical on palladium oxide. In this temperature range the analyses show that there is a slow evaporation of carbon dioxide but since the amount of adsorption continues to increase it is probably replaced by carbon monoxide, the dioxide being also adsorbed on palladium oxide but not on free palladium. In the higher temperature range the amount of adsorption decreases rapidly. Though the adsorption of carbon monoxide and carbon dioxide on palladium and of the dioxide on palladium oxide is negligible at 156° the carbon monoxide adsorbed on palladium oxide is quite strongly held at this temperature.

There are considerable data[9] which suggest that the reduction of platinum[10] oxide by carbon monoxide should be normal since it is adsorbed more strongly than hydrogen is by platinum, while the latter will displace carbon monoxide from palladium.[3a,11]

Summary

1. The adsorptions of oxygen, carbon dioxide and carbon monoxide on palladium oxide have been determined over the temperature range -78 to 218°.

2. Oxygen is not adsorbed by palladium oxide, nor by the oxide when partially reduced by carbon monoxide.

3. Carbon dioxide is adsorbed by palladium oxide reversibly, *i. e.*, by physical adsorption. The amount decreases with the extent of reduction of the surface of the oxide; on a sample only 2% reduced, the adsorption decreased by more than 50%.

4. The adsorption of carbon monoxide has a maximum about 100°. There is a physical adsorption at $-78°$. Activated adsorption increases slowly in amount between 0 and 100° and the gas is strongly held and evaporates only as carbon dioxide. Complete desorption occurs only above 218°.

5. The rates of adsorption on partially reduced samples and activation energies calculated from them indicate a complex process. Carbon monoxide is also adsorbed on the free palladium but so strongly that the further reduction of adjacent palladium oxide is not accelerated. The reaction does not occur at an interface, that is, it is not autocatalytic.

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(9) Langmuir, *Trans. Faraday Soc.*, **17**, 607, 621 (1921); THIS JOURNAL, **40**, 1361 (1918); Pollard, *J. Phys. Chem.*, **27**, 356 (1923); Harbeck and Lunge, *Z. anorg. Chem.*, **16**, 50 (1898).

(10) Baker and Company, Inc., Newark, New Jersey, have generously supplied a quantity of platinum for a similar investigation with that metal.

(11) Also De Hemptinne, *Z. physik. Chem.*, **27**, 429 (1898).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Preparation and Properties of Anhydrous Acetic Acid

BY WILLIAM C. EICHELBERGER AND VICTOR K. LA MER

Cryoscopic and solubility investigations with acetic acid as solvent require the preparation of anhydrous material of high purity in large quantities. The melting point must be highly reproducible without entailing undue labor.

The methods that have been employed may be summarized as follows: (1) repeated fractional crystallization,[1] followed by (a) distillation;[2] (b) drying with phosphorus pentoxide in the quantity calculated to react with the water present to form orthophosphoric acid and then distillation from the phosphorus pentoxide[3] (a small quantity of acetic anhydride is produced[3]); or (c) refluxing with the exact quantity of acetic anhydride required to convert the remaining water to acetic acid.[4] (2) Refluxing for one-half hour with two per cent. by weight of potassium permanganate and distilling from the residue.[5,6] We have found that such acid never melts above 16.55°. (3) Refluxing for ten hours with chromium trioxide[7] in an amount in excess of that calculated to react with the water present to convert it to chromic acid.[8]

The melting point is a good and frequently used criterion of purity but unfortunately only two laboratories[5,6] have reported how their thermometers were standardized, so that variations ranging from 16.4 to 16.60° may be due to inaccuracy in the temperature scale as well as to impurities.

We investigated methods (1a), (2) and (3). The first was very tedious when large quantities are needed. One fractional distillation with a good still yields acid of higher melting point than several recrystallizations. Potassium permanganate oxidized much of the acetic acid when applied to quantities of four liters or more. The chromic oxide method proved to be the most satisfactory.

Chromic Oxide Method.—Four liters of Niacet Chemical Company C. P. acetic acid (melting point 16.5°) was refluxed for about ten hours with an amount of chromium trioxide slightly in excess of that calculated to react with the water present to form chromic acid (about 1% by weight), assuming 16.60° to be the melting point of the pure acid and all the freezing point lowering to be due to water.[1] The acid was then distilled rapidly using an all-glass distilling apparatus protected by calcium chloride guards, followed by a careful fractionation with a two-foot Vigreaux column. After one liter had been distilled, the melting point of the distillate was 16.3°; it rose to 16.50–16.55° for the next liter, and to 16.57–16.60° for the remainder. Other workers[6,7,8] using this or the potassium permanganate method report a melting point of 16.55° for the second and third quarters of the distillate. One purification using two per cent. chromium trioxide yielded acid of the same purity but more of the low-boiling fraction, indicating that more water had been formed and hence more acid decomposed.

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(1) De Visser, *Rec. trav. chim.*, **12**, 101 (1893); m. p. 16.5965°.

(2) Conant and Werner, THIS JOURNAL, **52**, 4436 (1930); m. p. 16.4 to 16.6°; Hall and Voge, *ibid.*, **55**, 239 (1933); m. p. 16.63°, $\kappa = 3 \times 10^{-8}$ mhos at 25°.

(3) Orton, Edwards and King, *J. Chem. Soc.*, **99**, 1178, 1181 (1911); m. p. 16.4 to 16.51°.

(4) Kendall and Gross, THIS JOURNAL, **43**, 1426 (1921); m. p. 16.57 ± 0.05°; $\kappa = 2.4 \times 10^{-8}$ mhos at 25°.

(5) Bousfield and Lowry, *J. Chem. Soc.*, **99**, 1432 (1911); m. p. 16.60 ± 0.005°. Thermometer calibrated at Reichsanstalt and National Physical Laboratory.

(6) MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932); m. p. 16.54 ± 0.01°. Thermometer calibrated against resistance thermometer certified by Bureau of Standards; $\kappa = 1.4 \times 10^{-8}$ mhos at 25°.

(7) Hutchison and Chandlee, *ibid.*, **53**, 2881 (1931); m. p. 16.55°.

(8) Harned and Ehlers, *ibid.*, **54**, 1350 (1932); m. p. 16.55°.

Triacetyl Borate Method.—Triacetyl borate[9] is an excellent dehydrating agent for purifying acetic acid which has apparently escaped attention. It reacts with water to yield acetic acid and insoluble boric acid which may be completely separated in the final distillation: $B(OCOCH_3)_3 + 3H_2O = 3CH_3COOH + B(OH)_3$.

Triacetyl borate was prepared according to the directions of Pictet and Geleznoff[10] by warming to 60° a mixture of boric acid (powdered) and acetic anhydride in the ratio of 1:5 parts by weight: $B(OH)_3 + 3(CH_3CO)_2O = B(OCOCH_3)_3 + 3CH_3COOH$. On cooling, most of the triacetyl borate precipitates and is removed on a suction filter. It is very hygroscopic.

The purified acetic acid was refluxed with the triacetyl borate in the all-glass apparatus and then carefully distilled. Two to four times the amount of triacetyl borate calculated to react with the water present was used. Acetic acid of the same melting point was always produced. If four liters of the acid was dried at one time, two and a half to three liters was collected with a variation of not over 0.02° in the melting point, that is, from 16.58–16.60°.

This value was determined with a thermometer calibrated against a copper–constantan thermocouple, standardized against the fixed points of 0°, 32.384 ($Na_2SO_4 \cdot 10H_2O$) and a platinum resistance thermometer certified by the Bureau of Standards. The specific conductance (κ) of the acid was measured at the Rockefeller Institute with apparatus placed at our disposal by Dr. D. A. MacInnes, and yielded a value of 1.4×10^{-8} mhos at 25°.

Conclusions

Methods of purifying pure, anhydrous acetic acid in large quantities are discussed. Oxidation with chromium trioxide to remove impurities followed by dehydration with triacetyl borate was found to be the most satisfactory method.

The melting point of pure anhydrous acetic acid is 16.60 ± 0.01° and the specific conductance is 1.4×10^{-8} mhos (25°).

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[9] Suggested by Dr. Donald MacGillavry of this Laboratory who has made a preliminary investigation.

[10] Pictet and Geleznoff, *Ber.*, **36**, 2219 (1903).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Analytical Determination and Conductance of Sulfuric Acid in Anhydrous Acetic Acid

BY WILLIAM C. EICHELBERGER AND VICTOR K. LA MER

An accurate method of analyzing very dilute solutions of sulfuric acid in anhydrous acetic acid is essential for cryoscopic studies of such solutions. The customary acid-base titration is impossible because of the acid nature of the solvent. Gravimetric determination as barium sulfate is not feasible because of the possibility of adsorption of acetic acid on the precipitate. The corresponding conductivity titration, however, yielded a satisfactory analytical method. To avoid the introduction of foreign ions which would disturb the conductivity, barium acetate was selected as the source of barium ion.

The specific conductances of acetic acid–water mixtures were investigated to find the most suitable dilution where the errors caused by absorption of moisture during titration are at a minimum. The specific conductances (Table I) when plotted against percentage of acetic acid (Fig. 1) yield a curve with a maximum at about 18% acetic acid, which falls off sharply on each side of this point, flattening out at about 80% acetic acid with an asymptotic approach to the abscissa. An 18% solution should therefore be least sensitive to variations in water content. Unfortunately, the conductivity titration curves for this solvent yielded a poorly defined intersection (Fig. 2A). For a solvent of 50% acetic acid and 50% water, the initial points obtained with small additions of the barium acetate solution when plotting the reciprocal of the resistance against the amount of solution, fell on a straight line (Fig. 2B), but after the equivalence point was passed all the points were on a curve. The conductivity titration curves obtained in 75% acetic acid to 25% water mixture yielded an intersection sufficiently well defined to give a precision of two or three parts per thousand (Fig. 2C).

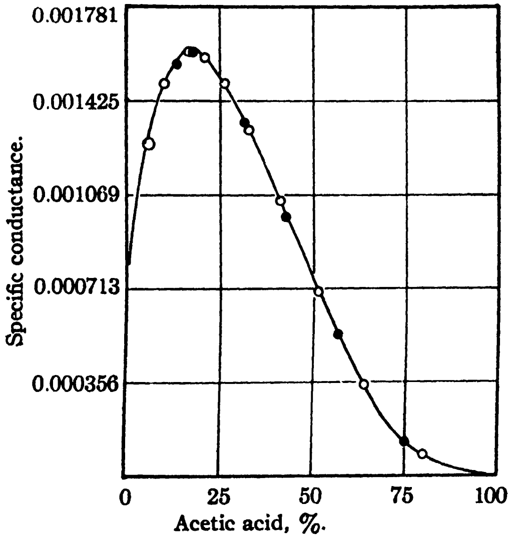

Fig. 1.—Specific conductance of acetic acid–water mixtures.

A conductivity cell of 200 cc. capacity with electrodes 1 sq. cm. in area is suitable for titrations of 0.005 molal sulfuric acid (the most dilute analyzed). The barium acetate solution was prepared by dissolving Kahlbaum C. P. barium hydroxide in the calculated amount of pure acetic acid and water, and was standardized conductimetrically in the same manner as it was to be used. The final procedure involved placing 50 cc. of 0.01000 *M* aqueous sulfuric acid in the conductivity cell, adding 150 cc. of pure acetic acid—a considerable contraction in volume occurs—and titrating the contents with 0.5 *M* barium acetate solution from a weight buret in approximately 100-milligram portions.

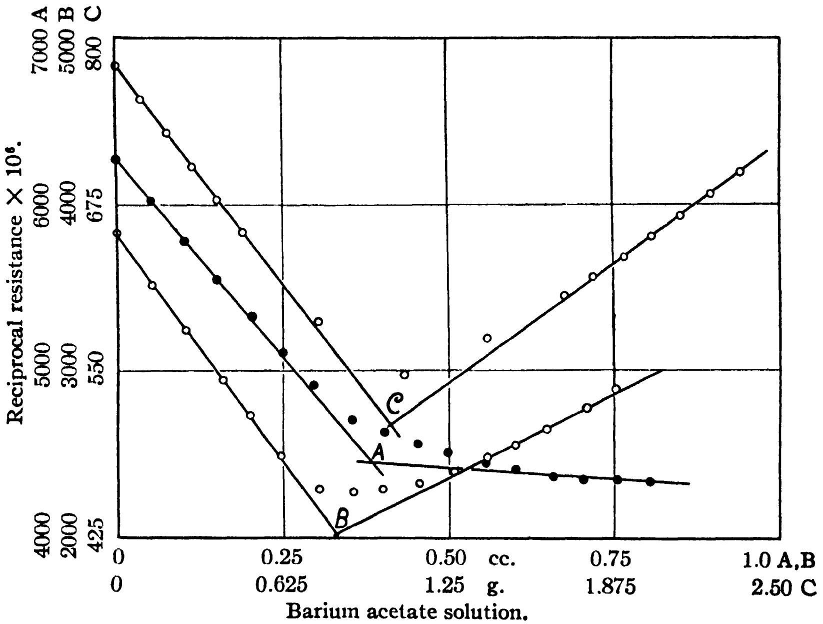

Fig. 2.—Conductivity titrations of sulfuric acid in: (a) 20% acetic acid–80% water; (b) 50% acetic acid–50% water; and (c) 75% acetic acid–25% water solvents.

The exact point of intersection was determined algebraically from the equations fitting the linear portions of the experimental curves of the type illustrated in Fig. 2C.

It is important that the determination of the unknown be carried out under approximately the same conditions as employed in standardizing the known solution, because of "electrolyte effects." Thus, if the concentration of the sulfuric acid was doubled, the barium acetate required would not be exactly twice that for the first solution. However, if the concentrations of sulfuric acid in duplicate experiments agreed to within 5%, the titers checked to 0.2%. The resistances of the known and un-

TABLE I

SPECIFIC CONDUCTANCE OF ACETIC ACID–WATER MIXTURES AT 25°

Acetic acid, %	Specific conductance, mhos
Series A	
100	1.4×10^{-8}
75	0.000136
56.2	.000537
42.2	.000984
31.6	.001333
23.7	.001392
17.8	.001611
13.3	.001563
Series B	
100	1.4×10^{-8}
80	0.000077
64	.000346
51.2	.000700
41.0	.001042
32.8	.001312
26.2	.001492
21.0	.001588
16.8	.001613
10.1	.001492
6.0	.001260

TABLE II

MOLAL CONDUCTANCE AT 25° OF SULFURIC ACID IN ANHYDROUS ACETIC ACID

(M. p. 16.60°; $\kappa = 1.4 \times 10^{-8}$ mhos)

Molality	Molal conductance
Series 1	
0.00502	0.106
.00496	.0842
.00946	.0686
.00987	.0701
.0494	.0498
.0510	.0530
.0982	.0701
Series 2	
0.1003	0.0707
.1001	.0748
.0481	.0552
Series 3	
0.01004	0.0730
.01947	.0543
.01948	.0540
.0369	.0507
.0400	.0532
.0795	.0560
.0805	.0557

known solutions must also agree within 10% of each other in order to obtain the precision desired. A preliminary determination is therefore necessary.

Conductance measurements also were carried out on solutions of sulfuric acid in anhydrous acetic acid. The results are given in Table II and plotted in Fig. 3. The curve follows the general type predicted by Walden[1] for solvents of low dielectric constant. A Washburn type of cell was used for these measurements.

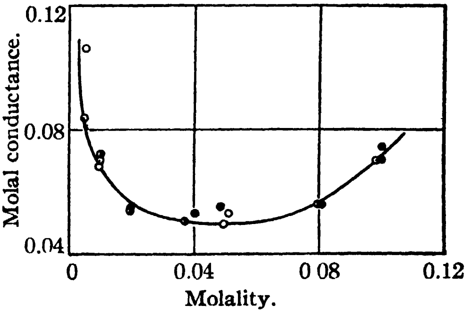

Fig. 3.—Molal conductance of sulfuric acid in anhydrous acetic acid.

Since completing this work (Spring, 1932), Hall and Voge[2] have published the complete conductance curve for the binary system H_2SO_4–CH_3COOH (m. p. 16.63° and $\kappa = 3 \times 10^{-8}$ mhos at 25°). Our curve parallels theirs very closely, but is displaced above it by an amount which would correspond to the presence

(1) Paul Walden, "Salts, Acids and Bases," McGraw-Hill Book Co., Inc., New York, 1929.

(2) Hall and Voge, THIS JOURNAL, 55, 239 (1933).

of only 0.02% water, if the source of the difference is attributed entirely to moisture. Our solutions stood for a few days in well-stoppered, ordinary glass bottles which had been used for acetic acid solutions for several months previously. They were protected by beakers sealed with paraffin.

The measurements were made on apparatus[3] of the a. c. bridge type consisting of the following parts: a 1000-cycle microphone hummer, a Kohlrausch slide wire (Leeds and Northrup Co.), non-inductive type resistance (Leeds and Northrup Co.), accurate to 0.05%, a variable air condenser across the resistance box to balance the capacity of the cell, and a two-stage audio amplifier with headphones matched to the frequency of the oscillator. The center of the bridge is grounded and all leads are shielded. The conductivity cell is placed in a thermostat which is constant to 0.005°.

Conclusions

1. A conductivity method is described for the precise determination of small quantities of sulfuric acid when dissolved in anhydrous acetic acid.
2. The specific conductances of the complete range of acetic acid-water mixtures have been determined.
3. The molal conductances of solutions of 0.005 to 0.10 *M* sulfuric acid in anhydrous acetic acid were determined. The data agree very well with the recent measurements of Hall and Voge.

[3] Kindly loaned to us by Professor J. J. Beaver of this Department.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Monochloroacetic Acid, at 25°, from Conductance Measurements[1]

BY BLAIR SAXTON AND THEODORE W. LANGER

In sufficiently dilute aqueous solution the thermodynamic ionization constant of a weak acid, HA, is given by the equation

$$K = \gamma^2 C_i^2/(C - C_i) = \gamma^2 K' \qquad (1)$$

where γ is the geometrical mean activity coefficient, C_i is the concentration of the ionized portion, and C is the total concentration of the acid. K' is the usual concentration (or dilution) constant. Evaluating γ by means of the limiting law of Debye and Hückel,[2] taking the dielectric constant for water at 25° as 78.56 (the mean of the results of Drake, Pierce and Dow[3] and Wyman),[4] we may write

$$\log K = \log K' - 1.013\sqrt{C_i} \qquad (2)$$

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[1] This paper contains material which represents part of the dissertation submitted by Theodore W. Langer to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931. The authors wish to acknowledge their indebtedness to Lawrence S. Darken and Harry F. Meier, who contributed the measurements on hydrochloric acid and its sodium salt.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[3] Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

[4] Wyman, *ibid.*, **35**, 623 (1930).

When C_i has been determined from conductance measurements, this equation has been verified by MacInnes and Shedlovsky(5) for acetic acid, Davies(6) for mandelic acid, and by our own results.

The ionic concentration can be determined from conductance data by means of the relation

$$C_i = \alpha C = \Lambda/\Lambda_{(H^+ + A^-)}\, C = 1000\, k\, (L/\Lambda_{(H^+ + A^-)}) \qquad (3)$$

where k is the cell constant and α, L, Λ and $\Lambda_{(H^+ + A^-)}$ are the degree of ionization, the cell conductance, the equivalent conductance and the sum of the equivalent conductances of the ions of the weak acid, respectively. For a given value of C_i, the denominator can be determined by the relation

$$\Lambda_{(H^+ + A^-)} = \Lambda_{(HCl)} - \Lambda_{(NaCl)} + \Lambda_{(NaA)} \qquad (4)$$

For very dilute aqueous solutions Λ for each of the strong electrolytes can be expressed as a function of C_i by means of the Debye–Hückel–Onsager(7) equation

$$\Lambda = \Lambda_0 - (0.2276\, \Lambda_0 + 59.88)\sqrt{C_i} \qquad (5)$$

Shedlovsky(8) has empirically extended this to more concentrated solutions, obtaining the equation

$$\Lambda_0 = \frac{\Lambda + 59.88\sqrt{C_i}}{1 - 0.2276\sqrt{C_i}} - BC_i = \Lambda_0' - BC_i \qquad (6a)$$

$$\Lambda = \Lambda_0 - (0.2276\, \Lambda_0 + 59.88)\sqrt{C_i} + BC_i(1 - 0.2276\sqrt{C_i}) \qquad (6b)$$

in which B is an arbitrary constant. Using this equation for each strong electrolyte an equation of the type of (6b) for $\Lambda_{(H^+ + A^-)}$ results through substitution in equation (4). Values of C_i, K' and K can then be computed from equations (3), (1) and (2), respectively. This method has been used successfully by MacInnes and Shedlovsky(9) in their work on acetic acid. Since the conductance data for each of our strong electrolytes is represented by equation (6b), we have also used this method.

Apparatus

The Bridges.—Two bridges were used. The first was a modified Jones and Josephs(10) type constructed from apparatus at hand in the laboratory. The Wagner ground consisted of a Kohlrausch slide wire and a General Radio type 219 G condenser. The ratio arms were a Leeds and Northrup Kohlrausch slide wire of the older, marble drum type. An a. c.–d. c. calibration showed that the a. c. error was very small for readings near the center of the bridge. The standard resistances were a Curtis coil and a bifilarly wound decade box, both from Leeds and Northrup, which were calibrated against similar boxes certified by the Bureau of Standards. An air condenser and a General Radio type 219 G condenser, shunted across the standard resistance, produced the correct phase relations. Current from the bridge was led through a transformer, thence to a two-stage amplifier and telephone. At all concentrations absolute silence was obtained. All measurements with cell A, the weak acid and its sodium salt, were taken with this bridge.

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(5) MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

(6) Davies, *ibid.*, **54**, 1698 (1932).

(7) Debye and Hückel, *Physik. Z.*, **24**, 305 (1923); Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927); *Trans. Faraday Soc.*, **23**, 341 (1927); *J. Phys. Chem.*, **36**, 2689 (1932).

(8) Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

(9) MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

(10) Jones and Josephs, *ibid.*, **50**, 1049 (1928).

All measurements with cell B, hydrochloric acid and its sodium salt, were made with the new Leeds and Northrup bridge which has been described by Dike.[11] The ratio arms and all resistances were carefully calibrated against standard resistances certified by the Bureau of Standards. The condensers built into the bridge were sufficient to produce the correct phase relations.

Cells.—Two cells were used: cell A for the weak acid and its sodium salt, and cell B for hydrochloric acid and its sodium salt. A diagram of cell A, drawn approximately to scale, is shown in Fig. 1 (A). It is made entirely of Pyrex. The flask is two liters in capacity. The electrodes are heavy platinum disks, 3.8 cm. in diameter, and are sealed through the glass by means of platinum tipped tungsten rods. The opening at the top of the cell is ground to fit the collar of a weight buret. Cell B is made of Jena "Geräteglas." Figure 1 (B), giving the lower section of this cell, shows the other essential difference in the construction of the two cells. The electrodes are 2.5 cm. in diameter and are supported by thin-walled platinum tubing. A tube, provided with a stopcock, is sealed into the bottom of the electrode compartment. Through this tube air, freed from carbon dioxide and ammonia, was blown through the water at the beginning of a run until the conductance remained sensibly constant. Both cells were well annealed and sufficiently aged. The electrodes in both cells are unplatinized in order to facilitate the transfer from one concentration or electrolyte to another and to avoid any possible effect on the weak acids. Our results indicate that accurate conductance measurements can be made with such unplatinized electrodes. That there is no serious capacitance to earth is shown by the fact that no change was noticed when the quantity of solution in the cell was varied from the amount necessary to barely fill the electrode compartment to an amount which filled the flask more than half full. With cell B, the capacitance correction given in equation (7) was negligible in the range of concentrations of hydrochloric acid and sodium chloride used.

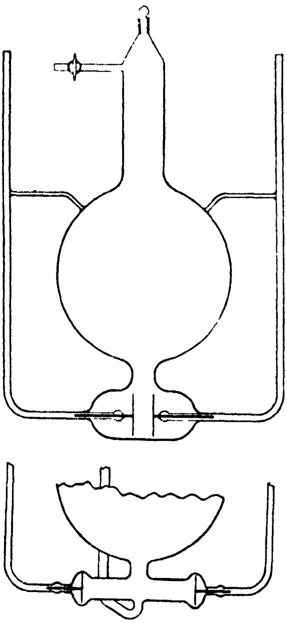

Fig. 1.—A, above; B, below.

Source of Power.—All recorded determinations were made at 1000 cycles generated by a shielded Vreeland oscillator situated about thirty feet from the bridge in another room. The low voltage secondary was connected to a potential divider, a manganin wire a meter long and of sixteen ohms resistance. By tapping about a millimeter from one binding post, a very low voltage was led directly to the first bridge. A somewhat greater voltage was sent through an intervening transformer to the second bridge.

Thermoregulation.—A rectangular porcelain thermostat, containing forty-five gallons of transformer oil, maintained a constant temperature. The bath was adjusted and its variation observed by a Beckmann thermometer which had recently been standardized against a platinum resistance thermometer. The temperature was 25.000 ± 0.005°.

Preparation of Materials

Conductivity Water.—For the measurements on the weak acid and its sodium salt, the water was obtained from a Barnstead automatic water still, electrically heated. The

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(11) Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

cooling water was so regulated that less than one-half of the steam condensed. The first four liters after starting were discarded. The water was distilled directly into the vessel in which it was to be used. With care, the specific conductance was 10^{-6} mhos. Except for some of the most dilute solutions, the water conductance was less than 1% of the total conductance.

For the measurements on hydrochloric acid and its sodium salt the water was obtained by redistilling distilled water containing alkaline potassium permanganate in a Barnstead "Conductivity Water Still" which is a modified form of that described by Kraus and Dexter.[12] In general it was distilled directly into the vessels in which it was used, but for storage a properly protected 15-liter "Vitreosil" retort was used. The specific conductance of the water so stored was 3×10^{-7} mhos, while that of water collected directly in cell B and subsequently treated with air freed from carbon dioxide and ammonia was $1-2 \times 10^{-7}$ mhos.

Acids.—Baker C. P. Analyzed special arsenic free hydrochloric acid was distilled twice from an all Pyrex glass still by trapping the hydrogen chloride gas which was driven off in water whose volume was one-third that of the acid introduced into the flask. Eastman's No. 68 monochloroacetic acid was distilled twice under diminished pressure. The product was a white solid melting at 62°. The cold solution showed no immediate turbidity with silver nitrate.

Salts.—For the cell constant determinations, Kahlbaum "Kaliumchlorid zur Analyse" was recrystallized four times from water. After drying for a day at 110°, it was fused in a platinum dish, then it was ground to a fine powder in an agate mortar. It was stored in a weighing bottle kept in a desiccator. A saturated solution of Baker C. P. Analyzed sodium chloride was dropped slowly into ethyl alcohol which had been distilled from lime. The precipitate was dissolved in water and the solution evaporated partially to reprecipitate sufficient salt. All the crystals were semi-dried by pressing and aspirating dust-free air over them. To prepare sodium monochloroacetate, the required amount of sodium carbonate was added slowly and with constant shaking to a known amount of the acid. The solution was neutral to litmus. The sodium carbonate was made from Merck C. P. sodium bicarbonate according to the directions in Treadwell-Hall.[13]

After being made alkaline with sodium carbonate and acidified with nitric acid, all solutions remained perfectly clear on addition of barium chloride, and all, except the chlorides, remained perfectly clear on addition of silver nitrate. The acids left no detectable residue when evaporated in platinum.

Experimental Procedure

The Conductance Measurements.—All measurements were in concentration series. A weighed amount of conductivity water was introduced into the cell, brought to the temperature of the thermostat and its conductance measured. Successive samples of analyzed stock solution were added with a weight buret, the solution thoroughly mixed, and after reaching the temperature of the thermostat, the conductance of the solution was determined. In each measurement the cell and standard resistance were reversed and the ratio again taken. With the first bridge, the ratio arms were kept as nearly as possible equal to unity, with the second bridge

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(12) Kraus and Dexter, THIS JOURNAL, **44**, 2469 (1922).

(13) Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1924, Vol. II, p. 475.

the ratio arms were always equal. The equivalent series resistance, R_4, of the cell was calculated from the equation[14]

$$R_4 = \frac{R_2}{R_1}\frac{R_3}{1 + R_3^2\,\omega^2\,C_3^2 + R_3\omega C_3\theta_3} \tag{7}$$

where R_1 and R_2 are the resistances of the ratio arms of the bridge, R_3 is the standard resistance, C_3 is the capacity of the condenser shunting R_3, and ω is 2π times the frequency. The last term in the denominator including θ_3, the phase difference in the condenser, is negligible except in the case of a few of the more concentrated solutions when measured in cell A. No change in the value of R_4, calculated from this equation, resulted when the frequency was changed from 1000 to 500. The whole water conductance was subtracted for the salts and neglected for the acids. The cell constants were determined with one hundredth demal potassium chloride prepared according to the directions of Parker and Parker.[15] Taking their value of 0.0014078_9 as the specific conductance, the cell constants are 0.07308 and 3.8503 for cells A and B, respectively.[16]

Determination of Concentrations.—The analyses of the stock solutions were calculated as the true weight of electrolyte per gram of solution weighed in air. Chlorides were weighed as silver chloride. In the case of sodium chloride this was checked against the value determined by synthesis. Monochloroacetic acid was titrated against sodium carbonate with sodium alizarin sulfonate as indicator. From the amounts used in preparation, the concentration of sodium monochloroacetate was calculated. Estimating the densities by interpolation, the concentration, in moles per liter of solution, was calculated.

Results

The measured equivalent conductances of the necessary strong electrolytes are expressed in equations (8), (9) and (11), and from these expressions equations (10) and (12) are derived.

$$\mathrm{H}^+ + \mathrm{Cl}^-;^{17} \quad \Lambda = 426.01 - 156.84\sqrt{C_i} + 169.7\,C_i(1 - 0.2276\sqrt{C_i}) \tag{8}$$

$$\mathrm{Na}^+ + \mathrm{Cl}^-;^{17} \quad \Lambda = 126.39 - 88.65\sqrt{C_i} + 94.8\,C_i(1 - 0.2276\sqrt{C_i}) \tag{9}$$

$$\mathrm{H}^+ - \mathrm{Na}^+; \quad \Lambda = 299.62 - 68.19\sqrt{C_i} + 74.9\,C_i(1 - 0.2276\sqrt{C_i}) \tag{10}$$

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(14) This relation, easily derived from the theory of the alternating current bridge on the assumption that R_1, R_2 and R_3 are reactance free, is essentially the same as equations (23) and (24) of Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

(15) Parker and Parker, *ibid.*, **46**, 312 (1924).

(16) Since this paper was written, Jones and Bradshaw [*ibid.*, **55**, 1780 (1933)] have reported new values for the specific conductances of potassium chloride. Their value for the 0.01 D solution is 0.062% higher than that given by Parker and Parker. If the new value be adopted, our cell constants and all our values of Λ should be increased by that amount, but our values of C_i, K' and K would be unaffected. The data of Shedlovsky, THIS JOURNAL, **54**, 1411 (1932), and of MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932), with which we later compare certain of our measurements, would only be raised by 0.028%, since their cell constants were determined with 0.1 D potassium chloride. In general, the agreement for the dilute solutions is improved in the cases of sodium chloride and sodium acetate, but is not improved in the case of hydrochloric acid.

(17) Determined by Lawrence S. Darken and Harry F. Meier in this Laboratory.

$$\mathrm{Na^+ + A^-};\quad \Lambda = 90.02 - 80.37\sqrt{C_i} + 67.7\,C_i(1 - 0.2276\sqrt{C_i}) \qquad (11)$$

$$\mathrm{H^+ + A^-};\quad \Lambda = 389.64 - 148.56\sqrt{C_i} + 142.6\,C_i(1 - 0.2276\sqrt{C_i}) \qquad (12)$$

Our experimental results are compared with those calculated from equations (8), (9) and (11) in Table I.

TABLE I

HCl

$C \times 10^3$	0.23042	0.45545	0.75166	1.3684	2.2406
Λ (obs.)	423.79	422.91	421.74	420.45	418.99
Λ (calcd.)	423.67	422.74	421.84	420.44	418.96
$C \times 10^3$	3.2561	4.5471	6.2065	8.0627	10.839
Λ (obs.)	417.59	416.18	414.68	413.26	411.51
Λ (calcd.)	417.61	416.19	414.69	413.27	411.48
$C \times 10^3$	15.063	20.055	24.822	31.097	
Λ (obs.)	409.25	407.09	405.35	403.40	
Λ (calcd.)	409.25	407.09	405.36	403.42	

NaCl

$C \times 10^3$	0.084837	0.33408	0.65245	1.4386	2.2142	
Λ (obs.)	125.61	124.90	124.28	123.17	122.44	
Λ (calcd.)	125.58	124.80	124.19	123.16	122.42	
$C \times 10^3$	3.2289	4.4206	5.7219	7.5809	8.3718	
Λ (obs.)	121.65	120.90	120.20	119.36	119.05	
Λ (calcd.)	121.66	120.91	120.22	119.38	119.06	
$C \times 10^3$	9.3286	11.443	13.845	15.883	18.784	22.299
Λ (obs.)	118.68	117.97	117.24	116.69	115.98	115.19
Λ (calcd.)	118.69	117.97	117.24	116.68	115.97	115.19

$CH_2ClCOONa$

$C \times 10^3$	0.6619	1.2613	1.8209	2.594	3.527
Λ (obs.)	88.17	87.12	86.68	86.12	85.43
Λ (calcd.)	88.00	87.25	86.71	86.10	85.48
$C \times 10^3$	4.039	5.005	5.841	6.496	7.077
Λ (obs.)	85.18	84.69	84.24	83.97	83.71
Λ (calcd.)	85.18	84.67	84.27	83.97	83.73

Our results for hydrochloric acid and sodium chloride are in good agreement with those of Shedlovsky[18] but are higher than those of Jeffery and Vogel.[19] From equation (12) and the conductances of monochloroacetic acid given in Table II, the remainder of the table was constructed.

If log ($K' \times 10^3$) be plotted against $\sqrt{C_i}$, the first six points, excluding the first, fall on a straight line, the equation of which is

$$\log (K' \times 10^3) = 0.1449 + 1.011\sqrt{C_i} \qquad (13)$$

From this it is apparent that nearly the theoretical slope has been obtained and that $K = 1.396 \times 10^{-3}$, which is the average of the first six values in Table II, again excluding the first value. Above 0.01 normal the curve falls below the limiting slope and the values of K decrease. This decrease

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[18] Shedlovsky, THIS JOURNAL, 54, 1411 (1932).

[19] Jeffery and Vogel, *J. Chem. Soc.*, (NaCl), 1716 (1931); (HCl), 400 (1932).

TABLE II

MONOCHLOROACETIC ACID

$C \times 10^3$	$L \times 10^3$	Λ	$C_i \times 10^3$	α	$K' \times 10^3$	$K \times 10^3$
1.814	5.593	225.32	1.062	0.585	1.500	1.390
4.048	9.675	174.67	1.844	.456	1.543	1.396
5.222	11.405	159.61	2.176	.417	1.554	1.394
6.230	12.765	149.74	2.438	.391	1.567	1.397
8.407	15.389	133.77	2.944	.350	1.587	1.398
9.464	16.525	127.93	3.164	.334	1.589	1.394
14.113	20.996	108.72	4.030	.286	1.611	1.389
18.824	24.866	96.54	4.782	.254	1.629	1.386
24.44	28.930	86.51	5.574	.228	1.647	1.384
30.19	32.615	78.95	6.293	.208	1.657	1.377

has been observed with acetic acid by MacInnes and Shedlovsky.[5] For both acids log K decreases approximately linearly with C_u, the concentration of the un-ionized acid. Further examples and a discussion of this relation will appear in a later paper from this Laboratory.

From a plot of log K' against $\sqrt{C_i}$ it is evident that equation (13) may be written

$$\log k' = \log K + a\sqrt{C_i} \tag{14}$$

where a in the dilute range approaches the theoretical value, 1.013, but decreases with concentration. Since $C_i^2/C_u = K'$, it follows that

$$\log K' = \log K + a(K')^{1/4}\, C_u^{1/4} \tag{15}$$

and since K' increases with concentration it may be expected that log K' should be a linear function of $C_u^{1/4}$, at least in the region of concentration in which the "medium effect" is not pronounced. This relation holds for monochloroacetic acid. If the acid is sufficiently weak, C_u may be replaced by C, the total acid concentration, and log K' and C_i may then be calculated from C. Even with an acid as strong as monochloroacetic the data can be represented by

$$\log (K' \times 10^3) = 0.1449 + 0.1794C^{1/4} \tag{16}$$

Excluding the first result, this equation reproduces the measured values of K' to within ±0.18% and the values of C_i to within ±0.07% and, therefore, gives a satisfactory method for calculating C_i from C. If this method be applied to MacInnes and Shedlovsky's[5] data on acetic acid, the results up to 0.01 N are given by the equation

$$\log (K' \times 10^5) = 0.24378 + 0.06074C^{1/4} \tag{17}$$

Above this concentration, the measured values of log K' fall below those calculated using equation (17) and the deviation is linear with C, which is to be expected if this is due to the "medium effect." Accordingly, a term in C was added to equation (17) giving

$$\log (K' \times 10^5) = 0.24378 + 0.06302C^{1/4} - 0.1256C \tag{18}$$

This equation reproduces K' to within ±0.10% and the values of C_i to within ±0.04%. It should be borne in mind that equations (16) and (18) reproduce the values of K' and C_i for the two acids, respectively, as measured by a conductance ratio in which $\Lambda_{(H^+ + A^-)}$ has been corrected for interionic forces but not for the presence of the un-ionized portion of the acid. More properly these are only apparent values except in the concentration range in which equation (2) is obeyed.

We have carried out similar measurements on acetic acid and its sodium salt in cell A. Our results agree with those of MacInnes and Shedlovsky[5] and not with those of Jeffery and Vogel.[20] Briefly, our results for sodium acetate are given by the equation

$$\Lambda = 90.91 - 80.57\sqrt{C_i} + 89.7C_i(1 - 0.2276\sqrt{C_i}) \qquad (19)$$

and our value of K is 1.759×10^{-5}. Our equivalent conductances for the acid are slightly higher than those of MacInnes and Shedlovsky.[5] This is probably due to the fact that our first conductivity water was not good enough for the measurements with such a weak acid. Their lower value, 1.753×10^{-5}, or 1.754×10^{-5} obtained by Harned and Ehlers[21] for electromotive force measurements is to be preferred.

Summary

Using a "flask" cell and bright platinum electrodes, the conductances of hydrochloric and monochloroacetic acids and their sodium salts have been measured and reported.

The results with all the strong electrolytes (those mentioned above and sodium acetate for which the equation only is given) confirm Onsager's equation as a limiting law, and up to our highest concentration, 0.03 N, agree with Shedlovsky's extension of Onsager's equation.

It has been shown that the theoretical constant of the limiting law of Debye and Hückel correctly represents the dependence of the activity coefficient of monochloroacetic acid upon its ionic concentration. Using this limiting law, the thermodynamic ionization constant of the acid is found to be 1.396×10^{-3}.

The values of the constant for acetic acid obtained by Harned and Ehlers and by MacInnes and Shedlovsky have been confirmed.

NEW HAVEN, CONNECTICUT

RECEIVED JULY 1, 1933
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[20] Jeffery and Vogel, *J. Chem. Soc.*, 2829 (1932).

[21] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932).

Notes

A Simple Automatic Pressure Regulator

By C. C. Coffin

One of the most satisfactory and convenient methods of obtaining constant temperatures in the laboratory is to use as a bath the vapor of a liquid boiling under a constant pressure. A pressure regulator is therefore necessary for accurate work with this type of thermostat particularly if the desired temperature corresponds to a vapor pressure much below one atmosphere. If the liquid is mercury, for example, a pressure change of 0.1 mm. at 200° (17.3 mm. Hg) corresponds to a temperature change of 0.17°. At 350° (697.8 mm. Hg) a pressure variation of 0.1 mm. produces a change of only 0.008°. The need of accurate pressure control at the lower pressures is obvious.

The purpose of this note is to describe a simple pressure regulator which has been found to be very satisfactory. It has been used particularly for obtaining constant temperatures between 210 and 280° with the vapor of boiling mercury[1] and would appear to the writer to possess certain advantages over some other regulators[2] which invariably involve the annoyance of mechanically operated valves to vacuum or pressure.

The operation of the regulator is made obvious by the accompanying diagram. The tube A connects with the space above the boiling mercury and with a 20-liter stabilizing volume the pressure changes in which move the manometer M to operate a relay R controlling the nichrome heating coil C. To set the apparatus in operation the pressure in the system is brought by means of tap B to a value slightly less than that desired and the amount of mercury in the manometer is adjusted by taps G and H until the surface on the vacuum side is slightly below the platinum point F. The switch S is then closed, C heats, and when contact is made at F the relay operates to break the heating circuit. The gas in D then cools, contact at F is broken and the cycle is repeated. The amount of mercury in M and the current in C should be adjusted to the rate of cooling of D so that the times of "make" and "break" are approximately equal. This

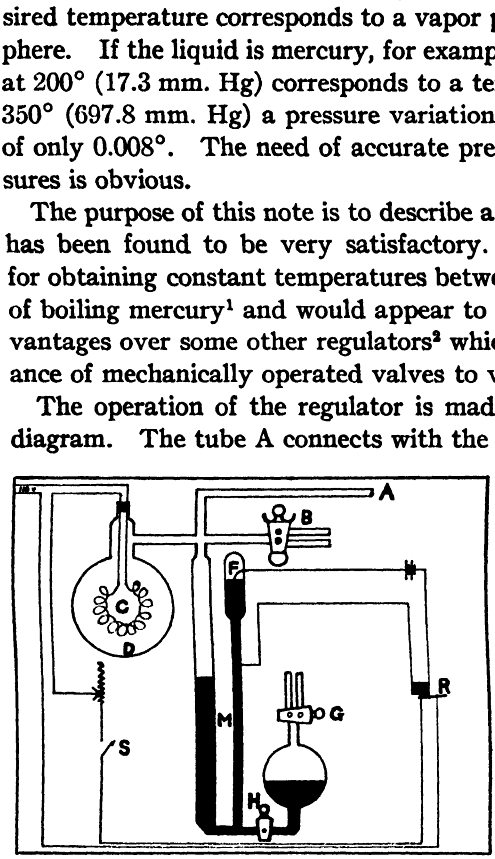

Fig. 1.—Automatic pressure regulator.

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[1] C. C. Coffin, *Can. J. of Research*, **5**, 636 (1931); **6**, 417 (1932); **7**, 75 (1932).

[2] Mathews and Faville, *J. Phys. Chem.*, **22**, 3 (1918); D. F. Smith, *Ind. Eng. Chem.*, **16**, 22 (1924); Carroll, Rollefson and Mathews, This Journal, **47**, 1791 (1925).

time should be long enough (several seconds) to prevent the manometer from building up a periodic oscillation.

When in operation the movement of the mercury surface at F is too small to be observed. Temperature measurements on a platinum thermometer in the mercury vapor at about 200° indicated that the pressure remained constant to well within 0.01 mm. while the temperature of the stabilizing volume was varied some 5°. The maximum change in room temperature that the heater can compensate for is, of course, dependent on such factors as the coil dimensions, the power input and the fraction that D is of the total volume. The fact that the control manometer is influenced by changes in room temperature introduces a slight error which, in precision work, could be avoided by the use of a thermostat.

This simple regulator should prove to be useful in many cases where a constant high or low pressure is required.

Other applications of an electrically heated wire in the construction of automatic laboratory devices will be discussed elsewhere.

CONTRIBUTION FROM THE
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Adaptation of the Dimethylglyoxime–Benzidine Test for Cobalt to the Usual Scheme of Qualitative Analysis

BY ALFRED W. SCOTT

A. Chiarothino[1] states that a solution containing cobalt when treated with an alcoholic solution of dimethylglyoxime and benzidine gives an orange-red color. It is further stated that this test must be carried out in a neutral solution.

In nearly all schemes of qualitative analysis the cobalt and nickel precipitate, or the solution obtained from it, is divided into two parts in order to run confirmatory tests for these two cations. The author thought that if the dimethylglyoxime–benzidine test could be adapted to the usual scheme of analysis it might be of advantage since all of the cobalt and nickel precipitate could be used for each test. The following procedure, suitable for use in the ordinary scheme of qualitative analysis, was found to give satisfactory results even when the concentration of nickel was fifty times that of cobalt.

The precipitate of cobalt and nickel sulfides, after separation from the rest of the group three precipitate, is dissolved in hydrochloric acid containing a little nitric acid. The solution is filtered and the filtrate evaporated practically to dryness. The residue is dissolved in a few cc. of water containing 1 cc. of dilute acetic acid. To this solution is added 1 g. of solid

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(1) A. Chiarothino, *Industria Chimica*, 8, 32 (1932).

sodium acetate, 0.5 cc. of a 0.5% alcoholic solution of benzidine and an excess of an alcoholic solution of dimethylglyoxime. If nickel is present the solution is filtered. In the absence of cobalt the filtrate will be colorless to yellow. If cobalt is present the filtrate will have a red coloration. Should the concentration of cobalt be so small that the red color is not very pronounced, it may be intensified by adding solid sodium acetate and allowing to stand for several hours.

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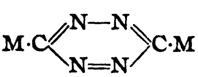
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

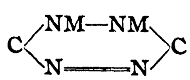
Tetrazine[1]

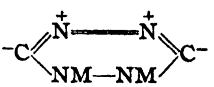
BY DENNISTOUN WOOD, JR., AND F. W. BERGSTROM

In connection with our attempts to prepare nitrogenous derivatives of divalent carbon,[2] we were interested by Müller's statement[3] that "1,2,4,5-tetrazine still contains two atoms of hydrogen which may be replaced by metals, and so have an acid character." In support of his statement, Müller has only his observation that tetrazine and silver nitrate form a precipitate of dark green needles,[4] but no analysis of this has been made.[5] On the other hand, Hantzsch and Lehmann[6] state that tetrazine forms no salts with either acids or bases, but that it reduces silver nitrate and mercuric chloride.

In view of these conflicting statements, it became desirable to see whether or not tetrazine[7] does form metallic salts corresponding to one or more of the formulas (M is a monovalent metal).







Preparation and Properties of Tetrazine.—Tetrazine was prepared from monochloroacetic acid through the following intermediates: glycine ethyl ester hydrochloride,[8] ethyl diazoacetate,[9] sodium bisdiazoacetate,[10] bisdiazoacetic acid,[8] tetrazine dicarboxylic acid.[11] Tetrazine[12] itself was prepared by heating an intimate mixture of its

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(1) Abstracted from the doctoral dissertation of Dennistoun Wood, Jr., Stanford University, 1930. Presented at the Denver Meeting of the American Chemical Society, August, 1932.

(2) Wood and Bergstrom, THIS JOURNAL, **55**, 3314 (1933).

(3) Müller, *Ber.*, **47**, 3001 (1914).

(4) Curtius, Darapsky and Müller, *ibid.*, **40**, 86 (1907).

(5) Müller, personal communication.

(6) Hantzsch and Lehmann, *Ber.*, **33**, 3678 (1900).

(7) Tetrazine is at the same time a derivative of formamidine (ammono formic acid), hydrazine and di-imide.

(8) Hantzsch and Silberrad, *Ber.*, **33**, 70–72 (1900).

(9) Curtius, *J. prakt. Chem.*, [2] **38**, 401–404 (1888); Silberrad, *J. Chem. Soc.*, **81**, 600 (1902).

(10) Curtius and Lang, *J. prakt. Chem.*, [2] **38**, 532 (1888).

(11) Curtius, Darapsky and Müller, *Ber.*, **40**, 1184 (1907).

(12) Curtius, Darapsky and Müller, *ibid.*, **40**, 84–85 (1907).

dicarboxylic acid with sand. A wad of glass wool is placed over the sand layer in the test-tube to prevent contamination of the tetrazine with undecomposed acid and sand. It is worthy of mention that we have found the yield of tetrazine to depend largely upon the length of time which the tetrazine dicarboxylic acid was dried in a vacuum, in conformity with the results of earlier investigators. The maximum amount obtained in this work was 16.8% of the theoretical. The total yield of tetrazine from 10 kg. of chloroacetic acid was only 7.9 g., or 0.18%, largely due to the fact that half of the dicarboxylic acid decomposed, apparently under the influence of radiant energy from a nearby muffle furnace.

Tetrazine itself is crimson colored, melting at 99° to a purple-red liquid. It is volatile even at room temperatures, and at higher temperatures is converted to a gas resembling iodine vapor in color. Its sharp irritating odor is also not unlike that of iodine. It has a bitter taste. Ethereal solutions of tetrazine cannot be concentrated even by vacuum distillation, because the solute volatilizes with the solvent. As will be shown later, liquid ammonia, maintained below −40°, is the only solvent from which tetrazine has ever been recovered. The solubility of tetrazine in water at 20° is roughly 6 g. in 100 cc. The solutions, even in great dilution, are pink.

As a general rule, it is essential to use tetrazine immediately after its preparation, but a pure specimen may be kept without decomposition for many months if sealed in a tube under its own vapor pressure. Left in air-filled tubes, even pure tetrazine becomes dark and pasty in a few hours, while the impure compound prepared from slightly moist tetrazine dicarboxylic acid, decomposes more rapidly. Much of the tetrazine may be recovered from the unpromising looking pasty mass by mixing it with barium oxide and resubliming. Dilute hydrochloric or sulfuric acid slowly decomposes tetrazine with evolution of gas (undoubtedly nitrogen) and conversion to a colorless solution. Very dilute ammonium or sodium hydroxide causes no apparent immediate change. In greater concentration, these alkalies together with potassium hydroxide turn tetrazine solutions brown, but ether extracts practically no color from them. Very little if any of the tetrazine is regenerated on acidification.

Tetrazine in its aqueous solution may best be recognized in the following manner. Hydrogen sulfide is passed through the ice cold solution until the pink color has changed to pale yellow, because of the formation of dihydrotetrazine.[13] Excess hydrogen sulfide is removed by a stream of nitrogen. A little ether and a few drops of sodium nitrite solution are added, the mixture is acidified with dilute acetic acid and shaken. The ether layer assumes a beautiful violet color from the regenerated tetrazine.

Reactions of Tetrazine outside of Ammonia.—Aqueous solutions of tetrazine produce no precipitate with picric acid, ferric chloride, lead dichloride or mercuric cyanide. With silver nitrate, an unstable explosive gelatinous precipitate of variable composition is formed. Auric chloride and tetrazine react in water to form a buff-colored precipitate, with evolution of gas and the occasional formation of metallic gold. The analyses of the precipitate are inconsistent. Hot aqueous mercuric chloride is reduced to mercurous chloride. Chloroplatinic acid does not form a precipitate with tetrazine, but when the reagents are sufficiently concentrated there is a rapid evolution of gas, indicating decomposition. It is evident that tetrazine may act as a reducing agent, as might be anticipated since it is a derivative of hydrazine. With a diethyl ether solution of methylmagnesium iodide, tetrazine forms a precipitate, apparently of an addition compound, since no methane is evolved.

The Behavior of Tetrazine with Ammonia.—Tetrazine is colored a deep purple by a small amount of ammonia at room temperature, but in a rapid stream of this gas it soon becomes pasty, occasionally hardening again in the ammonia atmosphere. The product, whose nature we have not been able to ascertain, explodes when rubbed with a

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(13) Curtius, Darapsky and Müller, *Ber.*, **40**, 86, 815–837 (1907).

glass rod. It dissolves readily in liquid ammonia, usually with a purple color, which may alter on standing. After evaporation of the solvent there remains a brick-red to purple imperfectly crystalline residue, a number of analyses of which are included in Table I.

Pure tetrazine dissolves readily in liquid ammonia at −40°. The more concentrated solutions are dark brown, the very dilute solutions pale buff, and the intermediate ones deep blood-red.

When a liquid ammonia solution of tetrazine which has been kept constantly at −40° or below is evaporated dry in a vacuum, a purple or copper-red substance is left in which are imbedded numerous small red crystals. These latter have been positively identified as unchanged tetrazine. The purple or copper-red material seems to be tetrazine coated with a thin film of the substances formed by the reaction of tetrazine with gaseous ammonia.

In Table I are summarized the analyses of a number of specimens of tetrazine, treated with gaseous or liquid ammonia at various temperatures. The extent of the decomposition of the specimens may be judged by an inspection of the analyses, since, theoretically, none of the nitrogen of tetrazine can be determined by the Kjeldahl method[14] (actually, see preparation 5).

TABLE I

Specimen Number	I	II	III	IV	V
% "Kjeldahl" Nitrogen	20.2	19.0	18.9	3.7	6.0

SPECIMEN I.—Tetrazine added to liquid ammonia at −40°, and solution allowed to stand at room temperature overnight.

SPECIMEN II.—Same as above, but solution allowed to stand at room temperatures for five to six hours.

SPECIMEN III.—Liquid ammonia distilled onto the purple product formed by the action of ammonia gas on tetrazine; solution allowed to stand for one day.

SPECIMEN IV.—Tetrazine added to liquid ammonia at −40°, and solution kept at this temperature until evaporated dry in a vacuum.

SPECIMEN V.—Pure tetrazine, not treated with ammonia.

The Reaction with Potassium Amide.—The reaction of tetrazine with potassium amide in liquid ammonia solution is carried out in Faraday tubes of the type described by Franklin[15a] and by Schurman and Fernelius,[16] in accordance with the technique first developed by Franklin and his co-workers.[15]

The addition of potassium amide to an excess (1.5 moles) of tetrazine causes the formation of a dark brown solution, from which nothing definite was isolated. The reverse addition of tetrazine to potassium amide in excess of 2 equivalents results in the precipitation of a substance approximating a dipotassium salt, $C_2N_4K_2$, in composition. If prepared in the customary manner from tetrazine that has reacted with liquid or gaseous ammonia at room temperatures, there are obtained gray-green to dark brown curdy or stringy precipitates, which usually can be hydrolyzed by water vapor without accident, giving solutions from which only relatively small amounts of tetrazine can be recovered. Since dilute sulfuric acid slowly decomposes these solutions with the formation of some hydrocyanic acid, it is concluded that the potassium salt, prepared in the described manner, is for the most part not a true derivative of tetrazine.

The decomposition of the dipotassium tetrazine is largely prevented if it is prepared and washed at a low temperature. To this end, tetrazine is dropped into liquid ammonia

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(14) Curtius, Darapsky and Müller, *Ber.*, **40**, 1176–1193 (1907).

(15) (a) Franklin, THIS JOURNAL, **27**, 831–833 (1905); (b) **35**, 1460–1462 (1913); (c) *J. Phys. Chem.*, **15**, 511–517 (1911).

(16) Schurman and Fernelius, THIS JOURNAL, **52**, 2428 (1930).

maintained around −40° by an external bath. The ammonia is contained in one leg of a reaction tube described by Schurman and Fernelius,[16] the other leg containing a solution of an excess of potassium amide, likewise cooled to −40°. With the addition tube sealed shut, the tetrazine is slowly poured into the potassium amide solution, producing a blood-red finely divided crystalline precipitate. This is thoroughly washed with liquid ammonia, still taking care that the temperature of the solvent does not rise above its normal boiling point. The legs of the reaction tube are separated, the precipitate leg evacuated at room temperature, the substance moistened with dry benzene, then hydrolyzed with moist benzene, and finally with water. A trace of air or of the vapor of air-free water invariably explodes the compound, and even a slight shock may detonate it. The explosions are remarkably violent, and may prove disastrous out of all proportion to the small amount of material involved.

That the blood red crystalline precipitate obtained in this manner is a true derivative of tetrazine is shown by the addition to this salt of an excess of cooled ammonium bromide solution, all reactants necessarily being held at a temperature of −40°. The precipitate dissolves to form a dull red solution, from which the solvent is removed by evaporation under diminished pressure. From the reddish purple solid, crystals of tetrazine are sublimed and condensed on a portion of the tube cooled by a swab dipped in liquid ammonia; m. p. 96–97°. The reduction–oxidation test, previously described in this article, likewise shows the presence of tetrazine.

TABLE II

ANALYSES OF THE PRECIPITATES FORMED BY THE ACTION OF TETRAZINE ON AN EXCESS OF POTASSIUM AMIDE

Specimen No.	I	II	III	IV	V	VI	VII	VIII	IX	X
Moles KNH_2 per mole tetrazine[a]	2.79	3.30	3.34	3.50	7.4	3.30	2.40	2.5	3.75	3.75
% K	45.2	52.7	45.5	50.0	49.0	54.0 50.6	49.8	45.6	48.5	51.4
% "Kjeldahl N_2"[b]	14.9	15.3					23.6			

Average: K, 49.4. Calcd. for $K_2C_2N_4$: K, 49.4, "Kjeldahl Nitrogen" 0.0. Calcd. for $C_2H_2N_4\cdot 2KNH_2$: K, 40.7.

[a] Reagents used in the reaction. [b] The Kjeldahl nitrogen is a quantity that cannot be calculated, since hydrolysis of the salt gives locally a high concentration of potassium hydroxide, which decomposes tetrazine in an unknown manner. Kjeldahl N is higher in the salts in which some previous decomposition is known to have occurred (No. VII).

Specimens I to VI were prepared from the cold solution of tetrazine in liquid ammonia. They were therefore all blood-red precipitates, except the second specimen VI. Specimen I was prepared with as great speed as possible at −40°. Specimens II to V stood overnight covered by liquid ammonia at room temperatures. Specimens VI were the products of continued washing of the precipitated salt with liquid ammonia. The upper analysis was of the red residue less soluble in ammonia, the lower analysis of the yellow substance left by evaporation of the wash liquid. Specimens VII to X were prepared from solutions of tetrazine which had reacted with ammonia, and so were brown or green precipitates. Specimen VII was made from tetrazine which had stood in liquid ammonia for seventy hours. Specimens VIII to X were made from tetrazine which had reacted with gaseous ammonia before being dissolved in the liquid.

The Reaction of Alkyl and Aralkyl Halides with Dipotassium Tetrazine.—The freshly prepared, and therefore reactive, salt of tetrazine explodes violently when exposed to methyl iodide vapor. Potassium cyanide is found among the reaction products.

Benzyl bromide reacts readily with the undecomposed salt in liquid ammonia solution, but no definite products were isolated.

Decomposition of Dipotassium Tetrazine under Liquid Ammonia.—When the blood-red dipotassium salt of tetrazine is allowed to stand for some hours under liquid ammonia at room temperature, the supernatant liquid becomes yellow, and the precipitate, while still explosive, has lost some of its sensitiveness. It may be safely hydrolyzed with water vapor. In the evaporation of a sulfuric acid solution of the substance some hydrazine sulfate appears to be formed.

In order to accelerate its decomposition, the dipotassium salt from 2.56 millimoles of tetrazine was heated for seven hours at 95–100° in liquid ammonia,[17] 2.50 millimoles of N_2 and 0.38 millimole of H_2 were obtained. The hydrolysate of the buff-colored precipitate could not be shown definitely to contain tetrazine, but a small amount of hydrazine was formed and identified by conversion to benzalazine. No N-aminotriazole was found.

Attempts to Synthesize Tetrazine by Other Methods.—Formimidoethyl ester hydrochloride, $H\cdot C(=NH)OC_2H_5\cdot HCl$, reacts with an aqueous solution of hydrazine hydrate and potassium hydroxide, or with a solution of hydrazine in liquid ammonia, to form small amounts of dihydrotetrazine, which are oxidized to tetrazine by atmospheric oxygen. The tetrazine was recognized by qualitative test, since it could not be isolated.

Dibenzyl- and Diphenyltetrazine.[18]—Both of these substances are sparingly soluble in liquid ammonia but dissolve readily in solutions of sodium or potassium amide at −40° or room temperatures to form, respectively, a deep red, and a lighter colored orange solution. Some nitrogen is evolved at the same time. The results will be reported at a later date.

Summary

1. Tetrazine reacts with aqueous solutions of silver nitrate, mercuric chloride, auric chloride and chloroplatinic acid, but without the formation of metallic salts or of definite addition compounds. The salt is often reduced to free metal.

2. Tetrazine dissolves in liquid ammonia and may be recovered from it unchanged, if the solution be kept at or below −40°. Otherwise, decomposition occurs. A number of new properties of tetrazine have been described.

3. Potassium amide reacts with tetrazine in liquid ammonia at −40° to form a red, highly explosive ammonia insoluble salt, approximately $K_2C_2N_4$, from which tetrazine may be recovered. At higher temperatures, the salt is slowly decomposed.

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[17] Using the method of Blair, THIS JOURNAL, 48, 90–92 (1926).

[18] The authors are indebted to Mr. A. E. Gilmore for their preparation.

The Oxidation of 5-Keto-gluconic Acid with Nitric Acid in the Presence of Vanadium

BY W. E. BARCH

5-Keto-gluconic acid has been obtained by Boutroux and others[1] from glucose by means of certain oxidizing organisms (bacterium xylinum, bacterium gluconium, etc.). Kiliani[2] obtained it by chemical means from glucose, by mild oxidation with nitric acid. His method of preparation has been the source of the material used in the following.

Boutroux[2b] oxidized the acid with nitric acid and identified among the products of oxidation racemic acid, trihydroxyxyloglutaric acid, glyoxylic acid, and others.

It has been shown by Odell[3] that *d*-tartaric acid may be obtained by nitric acid oxidation, in the presence of vanadium, of common starch.

There will be an attempt to show, in future publications, that this means of oxidation offers certain advantages over that using nitric acid alone, or other oxidizing agents, in the study of the oxidative degradation of the monosaccharides, their acids, and other derivatives. A major portion of the original molecule may be recovered in the form of four carbon acids, (*d*-tartaric, *l*-tartaric, racemic or mesotartaric acids, dependent on the configuration of the starting material). These acids are readily followed analytically in the presence of each other and other products of oxidation which may be present.

5-Keto-gluconic acid was chosen as the subject of this preliminary paper because of the relative simplicity of the oxidation, and because of its application as a partial picture of the more complex oxidation of glucose itself.

It was the original intention to conduct the experiments with the free acid. It was found that the sirup obtained from the calcium salt of the acid by decomposition with oxalic acid was too unstable in the high concentration necessary for the oxidation. It rapidly turns black on standing a short time in the desiccator over sulfuric acid, swelling and evolving gas.

It was found, however, that the calcium salt itself was suitable for the purpose. It is quite easily obtained in the pure condition, and dissolves readily in the nitric acid used in the experiments. The calcium of the salt appears early in the oxidation as calcium oxalate and may be removed by simple filtration.

Discussion

The results of twelve oxidations are tabulated according to the analytical methods described in the experimental part.

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(1) Boutroux, (a) *Compt. rend.*, **102**, 924 (1880); (b) **127**, 1224 (1898); (c) Bertrand, *Ann. chim.* [8] **3**, 281 (1904); (d) Bernhauer and Schon, *Z. physiol. Chem.*, **180**, 232–240 (1929); (e) Herman, *Biochem. Z.*, **214**, 357–367 (1929); (f) Takahashi and Asai, *J. Agr. Chem. Soc. Japan*, **6**, 223–241 (1930).

(2) Kiliani, *Ber.*, **55**, 2817 (1922).

(3) A. F. Odell. U. S. Patent 1,425,605.

The experiments are calculated on the basis of percentage of total carbon recovered from the original starting material as 100%.

It will be noted that as much as two-thirds of the original acid may be recoverable in readily determined non-gaseous products.

The main products are tartaric, racemic, trihydroxyxyloglutaric, and oxalic acids as shown. The column labeled carbon dioxide may be considered a rough estimation only, as it includes only that gas formed under the reflux and does not include that formed on evaporating off the nitric acid *in vacuo*. It is of interest chiefly in Part 1 in which the nitric acid was entirely consumed during the refluxing. One carbon of the six original carbons in the ketogluconic acid being 16.67%, it will be noted that the percentage of the gas with different molecular proportions of nitric acid closely approximates molecular proportions.

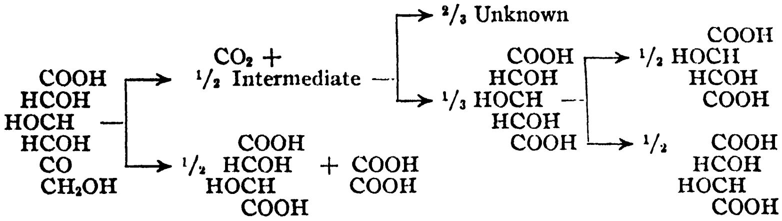
Referring first to Part 1, here the amount of available oxygen has been varied by varying the amount of nitric acid in each experiment. It has been a matter of observation, in this work, that at the boiling temperature nitric acid is deprived of oxygen by a simple reduction to nitrous acid, and therefore furnishes one molecular proportion of oxygen to one of nitric acid. This is true only at the higher temperatures, longer contact with the acid producing further reduction. In order to break the carbon chain at the keto group to tartaric and oxalic acids, or to trihydroxyxyloglutaric acid and carbon dioxide, three molecular proportions of oxygen are required. In this first series of four experiments, the following significant observations may be made. The greater bulk of the tartaric acid appears before any racemic or trihydroxyxyloglutaric acid can be detected. However, carbon dioxide, one-twelfth of the molecule (necessary for the postulation of one-half the original molecule breaking between carbon five and six) is formed at once. The amount shows no increase on increasing the molecular proportions of nitric acid from 2 to 2.5, indicating it as an early phenomenon. As tartaric acid continues to increase, the tryhydroxyxyloglutaric acid appears, oxidizing rapidly further to racemic acid. In the fourth experiment, with the splitting of the carbon chain presumably complete, the trihydroxyxyloglutaric acid has almost disappeared, the earlier formed tartaric acid has suffered by further oxidation, and the racemic acid is at its maximum point.

In Part 2, the available oxygen has been varied by time of contact with the nitric acid, using the same amount of nitric acid in each experiment. Here the peak for trihydroxyxyloglutaric acid is clearly shown, with its subsequent rapid disappearance.

All the products of the oxidation are themselves subject to further oxidation, making it probable that none of the observed results represent maxima. This is shown, to some extent, in Part 4, where the conditions of the oxidation are more mild than the foregoing. The amount of tartaric acid obtained here is near the maximum (33.3%) required by theory, and the trihydroxyxyloglutaric acid is also increased.

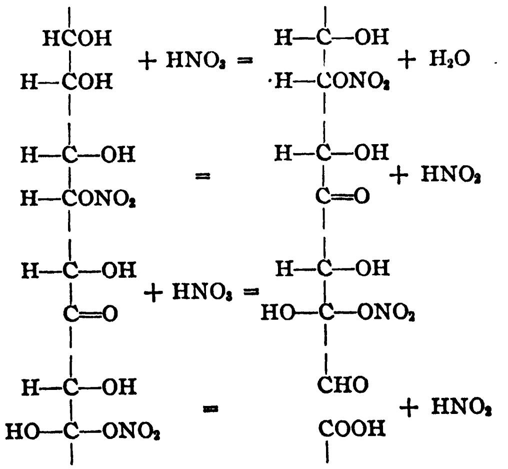
Summarizing, briefly, the following conclusions may be drawn on the breakdown of the carbon chain in 5-keto-gluconic acid on oxidation with nitric acid in the presence of vanadium.

The chain breaks on either side of keto group, equally between the break between carbon four and five and the break between carbon five and six; 50% of the molecule appears as tartaric and oxalic acids. Only one-third of the five carbon fragment appears as trihydroxyxyloglutaric acid, which is subsequently further oxidized to racemic acid. In this way, two-thirds of the original keto-gluconic molecule has been accounted for, the fate of the remaining one-third being unknown.



It is probable that vanadium is catalytically manifested only by the early break of the carbon chain between carbon four and five. Although four-carbon acids have been reported as products of oxidation of hexose derivatives, without the use of this catalyst, it is probable that they are the result of a secondary oxidation of the first formed five-carbon acid, as illustrated by racemic acid in these experiments.

There is indirect evidence for the following hypothesis as to the reaction mechanism.



When glucose is oxidized under the conditions described in this paper, and the reaction slowed, by cooling, after the first violent phase, the unreacted nitric acid may be removed by repeated extraction with ether. The resulting liquor, free of nitric acid, when allowed to stand a short time in sunlight gradually warms until there is again a violent reaction with vigorous evolution of nitrogen oxides.

The hypothesis of successive formation of unstable nitrates and their decomposition by loss of nitrous acid is also supported by the predominance of nitrogen peroxide over nitrogen monoxide in the early stages of the reaction and the evolution of nitrogen monoxide only, in the latter stages when the free nitric acid has been consumed.

$$\text{(Early stage)}\quad HNO_2 + HNO_3 = H_2O + 2NO_2$$
$$\text{(Latter stage)}\quad 3HNO_2 = HNO_3 + H_2O + 2NO$$

Carbon Distribution %

Part 1. Experiments refluxed to completion

Moles HNO_3	Acid Tartaric	Acid Racemic	Acid trihydroxy-xyloglutaric	Acid Oxalic	Solids Detd.	Reaction CO_2
2	17.3	0.0	0.0	11.4	28.7	8.3
2.5	20.4	0.2	4.1	14.2	38.9	8.1
3	27.8	4.0	5.9	17.3	55.0	16.7
4	14.2	8.5	1.1	16.8	40.6	33.1

Part 2. Experiments with 4 moles of nitric acid refluxed for different periods with the excess nitric acid quickly evaporated off *in vacuo*

Time, minutes	Acid Tartaric	Acid Racemic	Acid trihydroxy-xyloglutaric	Acid Oxalic	Solids Detd.	Reaction CO_2
30	24.3	0.0	0.0	17.2	41.5	1.7
60	22.2	1.8	11.7	16.3	52.0	8.0
120	26.7	2.1	8.7	19.0	56.5	13.2
960	14.2	8.5	1.1	16.8	40.6	33.1

Part 3. Experiments refluxed for thirty minutes with nitric acid and evaporated *in vacuo*

Moles HNO_3	Acid Tartaric	Acid Racemic	Acid trihydroxy-xyloglutaric	Acid Oxalic	Solids Detd.	Reaction CO_2
4	24.3	0	0	17.2	41.5	1.7
5	21.1	4.0	11.7	16.3	53.1	8.4

Part 4. Experiment with 6 moles nitric acid refluxed for ten minutes and the excess nitric acid evaporated at 45° *in vacuo*

	Acid Tartaric	Acid Racemic	Acid trihydroxy-xyloglutaric	Acid Oxalic	Solids Detd.	Reaction CO_2
	29.1	2.7	13.9	20.5	66.2	....

Part 5. Experiment allowed to stand at 45° to completion

Moles HNO_3	Acid Tartaric	Acid Racemic	Acid trihydroxy-xyloglutaric	Acid Oxalic	Solids Detd.	Reaction CO_2
4	19.4	7.6	0.6	37.4	65.0	....

Part 6. Experiment with 6 moles of nitric acid refluxed for ten minutes, then the excess nitric acid removed with formic acid

	Acid Tartaric	Acid Racemic	Acid trihydroxy-xyloglutaric	Acid Oxalic	Solids Detd.	Reaction CO_2
	20.9	0.5	0	16.0	37.4	9.2

Experimental

Preparation of Calcium 5-Keto-gluconate.—The method of Kiliani is repeated here, with some variation.

One hundred grams of glucose is dissolved in 28 cc. of water in a 300-cc. Erlenmeyer flask. To this is added 52 cc. of concentrated nitric acid (this is approximately

1.5 mole). Any number of these preparations as described may be placed in a slowly circulating shallow bath at 20 to 25°. Working with larger quantities in a single lot is not advisable because of difficulties in cooling.

Fumes of nitrogen peroxide appear slowly after twenty-four hours and continue to evolve for several days. In a week's time the reaction has practically ceased, and the flasks may be removed.

One hundred grams of solid sodium acetate is added and stirred into the acid solution, until it has dissolved more or less completely, and then 25 g. of calcium chloride dihydrate, dissolved in a little water. The solution becomes rapidly darker in color and may show a haze of calcium oxalate. Crystallization begins after four or five hours and continues almost indefinitely. The product obtained after long standing, however, contains large quantities of calcium saccharate. The subsequent purification is easier, if the precipitate is filtered off after forty-eight hours.

The brown amorphous precipitate is redissolved in sufficient hydrochloric acid to be equivalent to the calcium present in the precipitate. The calcium oxalate will remain undissolved in the cold, and is filtered off, after adding norite. The filtered and decolorized solution is then neutralized to 85% of its total acidity with aqueous ammonia, care being taken to avoid local alkalinity which will again color the solution. The calcium keto-gluconate appears rapidly as a coarse crystalline meal and may be filtered in a few hours.

After a second recrystallization in this manner, a product was obtained, pure white in color, containing 11.66% CaO, calcd. for $Ca(C_6H_9O_7)_2—3H_2O$, 11.67%. One gram dissolved in the theoretical amount of hydrochloric acid plus 5%, and made up to 25 cc., shows α^{20}_D of $-11.69°$, which calculated to the free acid is $-14.43°$. It shows no loss in weight on drying in the oven at 100°; yield, 10–12%.

Oxidation.—All experiments were conducted in the same manner, using 10 g. of the above prepared salt in a 250-cc. round-bottomed flask with a reflux condenser ground to fit the flask. The salt was covered with sufficient water to be equivalent, by volume, to 25% of the nitric acid used in the experiment. 0.001 g. of sodium orthovanadate was present in each experiment. The top of the reflux condenser was connected to two wash bottles containing concentrated sulfuric acid to absorb the bulk of the nitrogen oxides and then to a bottle containing 40% potassium hydroxide, protected from the atmosphere with a long tube coarsely packed with soda lime. This last was for a rough estimation of the carbon dioxide formed, which was determined on an aliquot of the potassium hydroxide solution by the usual volumetric method.

The flask containing the nitric acid, salt, water and sodium orthovanadate was immersed completely in a water-bath and heated to 100° (except where otherwise mentioned).

The reaction proceeds in three stages. The colorless solution very slowly turns green, a few desultory bubbles appear, increasing rapidly in number until a violent reaction ensues, with large quantities of red nitrogen peroxide evolving from the surface of the solution. The violent reaction is very brief and is succeeded by a slower reaction which continues for several hours. In this phase the nitrogen peroxide ceases to be evolved and is replaced by a slower evolution of nitrogen monoxide. The reaction is complete after all evolution of gas has ceased. Early in the reaction, soon after the violent phase, calcium oxalate begins to appear, in unusually coarse, granular crystals. To ensure the complete removal of the nitric acid, each experiment was evaporated to dryness in the vacuum without removing from the reaction flask.

Analysis.—The dry material is dissolved in a small quantity of hot water and the insoluble calcium oxalate filtered off. The filtrate is collected in a 10-cc. volumetric flask; 1 cc. is taken for titration with *N*/5 alkali. The same titration sample is then used for an oxalic acid determination. The remaining portion of the filtrate is then neutralized with the calculated quantity of a strong solution of potassium hydroxide (cooling) and rendered acid again with concentrated hydrochloric acid equivalent to exactly one-half the amount of the potassium hydroxide. The potassium acid salts of tartaric and racemic acids precipitate immediately and are filtered off after standing for forty-eight hours. The precipitate is washed with 60% alcohol.

The resulting precipitate is dried in the oven at 100° for twelve hours. A 1-g. sample is titrated with $N/5$ potassium hydroxide, then made up to 25 cc. and polarized. From the titration of pure potassium acid tartrate (26.58 cc.), and the specific rotation of potassium tartrate (α^{20}_{D} + 27.58°), the relative amounts of potassium acid tartrate and racemate may be calculated, together with inert material (potassium chloride). The weight of the equivalent potassium used in neutralizing is, of course, added to the original 1 g., in calculating the specific rotation of the unknown salt.

The filtrate from the potassium acid salts is evaporated to remove the alcohol, and sufficient calcium chloride added to be roughly equivalent to the oxalic acid as determined previously. This solution is immediately filtered hot and the filtrate neutralized. To this filtrate is added a solution equivalent to 5 g. of calcium chloride and allowed to crystallize for two days. The calcium trihydroxyxyloglutarate crystallizes rather slowly, and should only be filtered after no more crystals appear on the sides of the beaker after scraping down. The salt contains two molecules of water. It is not quite pure, but for purposes of analysis was considered as such because of the rather large loss on recrystallization: CaO determined, 21.87%; calcd. 22.06%. The free acid obtained by breaking up the salt with oxalic acid has no polarization and readily crystallizes from water; it melts at 142–144° and titrates 55.1 cc. of $^1/_5N$ KOH, calcd. 55.5.

Summary

1. The probable mechanism of the breakdown of 5-keto-gluconic acid on oxidation with nitric acid in the presence of vanadium is shown.

2. The application of the method as a means for the study of the oxidation of other carbohydrate derivatives is suggested.

FLUSHING, L. I.

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Solubility of Inulin

BY E. YANOVSKY AND R. M. KINGSBURY

Such expressions as "insoluble" and "slightly soluble" applied to inulin are very common in the literature, but actual measurements recorded are very few. Some of the old fragmentary results on solubility of inulin in water and alcoholic solutions are recorded by Dragendorff,[1] von Lippmann,[2] and Prantl.[3] Wolff and Geslin[4] investigated the comparative solubilities of inulin from chicory and dahlia with the results in Table I.

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(1) Dragendorff, "Materialien zu einer Monographie des Inulins," St. Petersburg, 1870, pp. 54 and 66.

(2) Von Lippmann, "Chemie der Zuckerarten," 1904, p. 797.

(3) Prantl, "Das Inulin," München, 1870, p. 21.

(4) Wolff and Geslin, *Bull. soc. chim. biol.*, **2**, 19 (1920).

TABLE I

t, °C.			15	30	40	45	50
Soly., grams in 100 cc.	Inulin from dahlia	I	0.045	0.185	0.305	...	0.558
		II	.333	.575	.920	...	1.490
	Inulin from chicory	I	.225	.400	.975	1.160	1.737
		II	1.445	1.859	2.400	...	...

The first line in each case represents inulin crystallized from water, the second, inulin precipitated with alcohol. Crystallization with the aid of alcohol increases the solubility of both; the chicory inulin, however, still remains the more soluble. Somewhat more detailed data on the solubility of inulin are presented in the following pages.

Materials Used.—Inulin was prepared from dahlia roots and chicory roots by the usual method[5] of extracting the roots with hot water, treating the solution with neutral lead acetate, removing the excess of lead with hydrogen sulfide, and evaporating the solution to the crystallization point. The inulin thus obtained was recrystallized four times by dissolving in hot water, treating with decolorizing carbon, and precipitating with alcohol. The final products, as used in the experiments described below, were white powders. Cursory microscopic examination showed that chicory inulin was the more crystalline of the two, consisting almost entirely of the typical spherocrystals, whereas dahlia inulin appeared to be largely amorphous with a few spherocrystals here and there. The specific rotation of dahlia inulin was found to be $[\alpha]^{20}_{\mathrm{D}}$ −36.9°; that of chicory inulin was $[\alpha]^{20}_{\mathrm{D}}$ −34.6°. Dahlia inulin contained 0.06% ash, chicory inulin contained 0.12%. Dahlia inulin had 0.45% reducing sugar, chicory inulin had 0.55%.

Analytical Procedure.—In analyzing inulin, or mixtures of inulin and levulose, two factors must be considered. First, that inulin is not hydrolyzed completely with acids at room temperature,[6] and second, that levulose gradually decomposes on heating with acids. The procedure used was as follows: a number of solutions of carefully purified inulin and levulose were brought to 99–100° (in boiling water). To 20 cc. of solution 5 cc. of 2.313 *N* hydrochloric acid was added. At frequent intervals (from one minute up) solutions were taken out, cooled quickly in ice water, neutralized, and brought to definite volume. Reducing sugar was determined by the Munson and Walker method. From several series of determinations it was found that heating for fifteen to sixteen minutes is sufficient to hydrolyze all the inulin; the correction for levulose decomposed is 3.0%.

In converting glucose values from the Munson and Walker tables into levulose a uniform factor 0.915 was used, thus admittedly introducing a small, for our purposes, rather negligible, error.[7] Likewise no correction has been made for glucose found by several investigators[6,8] after acid hydrolysis of inulin but apparently not formed (or formed only in small quantities) on hydrolysis by inulase.[9]

In view of the fact that the values for cuprous oxide in some of our results were very low the Fehling solution used was checked several times during the progress of experiments, but at no time did a blank determination with 50 cc. of water give more than one milligram of cuprous oxide.

Solubility of Inulin in Water at 20°.—Mixtures of water and inulin were kept at

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(5) Woskressensky, *J. prakt. Chem.*, **37**, 309 (1846).

(6) Jackson and Goergen, *Bur. Standards J. Research*, **3**, 27 (1929).

(7) Browne, THIS JOURNAL, **28**, 439 (1906); Jackson and Mathews, *Bur. Standards J. Research*, **8**, 403 (1932).

(8) Tanret, *Bull. soc. chim.*, **9**, 200, 227, 622 (1893); Schlubach and Elsner, *Ber.*, **62**, 1493 (1929).

(9) Bourquelot and Bridel, *Compt. rend.*, **172**, 946 (1921); Pringsheim and Ohlmeyer, *Ber.*, **65**, 1242 (1932).

20 ± 1° in tightly stoppered flasks and shaken by hand several times each day. Samples were removed at intervals of several days, filtered, and analyzed for reducing sugars and inulin. The results, given in Table II, indicate clearly that there is a substantial difference in the solubility of dahlia and chicory inulins, the latter being considerably more soluble. The findings corroborate the results of Wolff and Geslin, although their actual figures are somewhat different from ours. The most interesting fact brought out is that, although the solubility of dahlia inulin remained apparently constant during the period of experiment, the chicory inulin showed a very gradual but decided decrease in solubility.

TABLE II

SOLUBILITY OF INULIN AT 20 ± 1° IN GRAMS PER 100 CC.

Time, days	Dahlia inulin Expt. I	Dahlia inulin Expt. II	Chicory inulin Expt. I	Chicory inulin Expt. II	Time, days	Chicory inulin Expt. I	Chicory inulin Expt. II
1	0.16	..	1.48	..	23	1.02	...
5	..	0.16	..	1.21	27	0.85	...
9	0.16	..	1.20	..	29		0.91
10	..	0.18	..	..	35		.94
13	..	..	..	1.09	40		.85
14	..	..	1.19	..	47		.80
20	0.16	0.15	1.00	1.01	54		.76

In the figures given above no correction has been made for the small amounts of reducing sugar found; there was no increase in reducing sugar during the course of the experiment. This statement applies to all subsequent results, unless otherwise stated. The rather low values for dahlia inulin solubility were checked by evaporating the solutions and drying *in vacuo* to constant weight. Two results (0.16 and 0.16) agreed well with those given in the table.

Since the results in Table II were obtained with inulin recrystallized with the aid of alcohol, and Wolff and Geslin obtained different results when inulin was recrystallized from water, we made similar experiments. Pure chicory inulin was recrystallized three times from water without the aid of alcohol. This inulin was soluble to the extent of 0.12 g. per 100 cc., and the value for solubility did not change during six weeks' observation. In a duplicate experiment a value of 0.13 g. per 100 cc. was obtained. The figures for similarly treated dahlia inulin were: 0.03 and 0.04 g. per 100 cc.

It appears therefore that there are two forms of inulin of entirely different degrees of solubility, and that the two forms of chicory inulin are different from the corresponding forms of dahlia inulin. The form of chicory inulin obtained by the usual method of recrystallization with the aid of alcohol seems to be the unstable modification, which gradually changes into the less soluble form.

That the stable less soluble modification of chicory inulin can be transformed into the unstable more soluble modification was shown by the following experiments. Chicory inulin having an unchanging solubility of 0.12 g. per 100 cc. was recrystallized (1) from water with an equal volume of alcohol added, and (2) from the same amount of water with four volumes of alcohol added. The solubility of the first product was found to be 0.52 g. per 100 cc., but it gradually decreased to 0.32 g.; the solubility of the second product was 1.17 g. per 100 cc. after four days, and this decreased gradually to 0.40 g.

Solubility at Other Temperatures.—Table III gives the results on solubility of inulin at 6°. The figures for dahlia inulin approach the limits of the accuracy of the method. The values for chicory inulin show a gradual decrease, but not as prominent, as was noted at 20°.

The data in Table IV show that at 39° the solubility of chicory inulin decreases in a shorter time than at 20°. The solubility of dahlia inulin remained stationary.

TABLE III

SOLUBILITY OF INULIN AT 6 ± 1°, IN G. PER 100 CC.

	Dahlia inulin		Chicory inulin	
Time, days	Expt. I	Expt. II	Expt. I	Expt. II
6	0.08	0.08	0.58	0.60
15	.02	.03	.52	.54
21	.02	.02	.51	.54
26	...	...	.49	.50

At this temperature a gradual increase in reducing sugar was noticed, and the figures of the table were corrected accordingly. The corrections were: for dahlia inulin, 0.17, 0.24 and 0.31; for chicory inulin, 0.33, 0.51 and 0.74.

TABLE IV

SOLUBILITY OF INULIN AT 39 ± 1°, in G. PER 100 CC.

	Dahlia inulin		Chicory inulin	
Time, days	Expt. I	Expt. II	Expt. I	Expt. II
5	0.55	0.50	4.08	4.39
8	.48	.57	3.80	3.73
12	.50	.48	3.00	3.28

Solubility in 50% Alcohol.—The usual laboratory procedure in the preparation of inulin requires precipitation of a water solution of inulin with alcohol. Knowledge of the solubility of inulin in alcoholic solutions is therefore of interest. Table V shows that only traces of dahlia inulin are dissolved in 50% alcohol. The gradual decrease in solubility of chicory inulin is not pronounced. The last column of the table represents results obtained by evaporating the solutions and drying to constant weight.

TABLE V

SOLUBILITY OF INULIN IN 50% ALCOHOL AT 20 ± 1°, IN G. PER 100 CC.

Time, days		5	9	10	20	22	23
Dahlia inulin	Expt. I	0.06	0.04	..	0.03	..	(0.04)
	Expt. II	.04	..	0.04	.03	..	(.04)
Chicory inulin	Expt. I	.11	.15	..	.11	.07	(.07)
	Expt. II	.11	..	.12	.06	.07	(.07)

Solubility in Presence of Levulose.—In nature inulin is always accompanied by variable amounts of free levulose. We have investigated the solubility of inulin in solu-

TABLE VI

SOLUBILITY OF INULIN IN PRESENCE OF LEVULOSE AT 20 ± 1°, IN G. PER 100 CC.

	Dahlia inulin		Chicory inulin	
Concn. of levulose in solvent	Levulose found	Inulin found	Levulose found	Inulin found
0.00	0.02	0.16	0.03	1.20
.24	..	..	.25	0.91
.49	..	..	.46	1.11
.96	0.95	.18	.92	1.09
1.91	..	..	1.90	1.00
2.84	2.90	.19	2.84	0.99
4.69	4.71	.23	4.74	1.05
9.11	9.18	.41	9.09	1.10
13.31	13.54	(.22)	13.31	1.08
17.27	17.30	.62	17.17	1.06
24.56	24.42	.94	23.80	1.37

tions of different concentrations of levulose, and the results are given in Table VI. It appears that the solubility of dahlia inulin gradually increases with the increase of levulose in solution. In 25% levulose solution the solubility of dahlia inulin is practically equal to that of chicory inulin. On the other hand, the presence of levulose (up to 25%) does not seem to affect the solubility of chicory inulin.

Solubility in Presence of Soluble Inulin.—The yield of inulin prepared from a plant is considerably below the amount present in the plant as determined analytically. The uncrystallizable material represents either the degradation products of inulin or some form of soluble inulin. Therefore, we measured the solubility of inulin in solutions of soluble inulin prepared from camas bulbs.[10] The results given in Table VII show that the soluble inulin under the conditions observed is without any effect upon the solubility of either dahlia or chicory inulin.

TABLE VII

SOLUBILITY OF INULIN IN PRESENCE OF SOLUBLE INULIN AT 20 ± 1°, IN G. PER 100 CC.

Time, days	1	5	9	10	14	20
Control soln. of soluble inulin	1.33	1.37	1.31	1.33	1.33	1.32
Dahlia inulin	..	0.12	0.11	0.16	..	0.16
Chicory inulin	..	1.29	1.23	..	1.10	.97

Separation of Inulin from Supersaturated Solutions.—In common with other carbohydrates inulin easily forms supersaturated solutions. The knowledge of the extent of separation of inulin from its supersaturated solution is, of course, of utmost importance in the preparation of inulin. The existence of supersaturated solutions of inulin was known to early investigators.[1] Kiliani[11] noticed that if inulin is dissolved at higher temperature and then cooled, more inulin remains in solution than one would expect from the solubility data. Similar observation had been made by Tanret.[8] No data, however, were given by either investigator. We took a mixture of inulin and water, and after slightly warming it to produce a supersaturated condition kept the mixture at 20°. The supersaturated solution of dahlia inulin with an initial concentration of about ten times its normal solubility gradually deposited inulin, but it did not reach the normal solubility during the seven weeks of observation (Table VIII). The solution of chicory inulin, which had initially about twice the normal solubility, reached its solubility level at 20° in three to four weeks' time.

TABLE VIII

SUPERSATURATED SOLUTIONS OF INULIN IN WATER AT 20 ± 1°, IN G. PER 100 CC.

Time, days	Dahlia inulin Expt. I	Dahlia inulin Expt. II	Chicory inulin Expt. I	Chicory inulin Expt. II
1	1.60	..	2.24	..
5	..	1.13	..	1.92
9	1.04	..	1.81	..
10	..	0.99	..	1.74
14	0.93	.90	1.68	1.65
24	.72	.73	1.41	1.43
35	.69	.67	1.20	1.12
42	.61	.59	1.08	1.05

In another experiment with chicory inulin we used the mother liquor from recrystallization of inulin. Pure inulin was dissolved in boiling water, and the solution kept overnight in a refrigerator. The separated inulin was filtered off next day. The mother liquor, which contained 5.83% inulin, was kept at 20°. The gradual decrease in concen-

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(10) Yanovsky and Kingsbury, THIS JOURNAL, 53, 1597 (1931).

(11) Kiliani, *Liebigs Ann. Chem.*, 205, 145 (1880).

tration of inulin in solution is shown in Table IX. The level of solubility at 20° was reached in four to five weeks.

TABLE IX

SEPARATION OF CHICORY INULIN FROM ITS SUPERSATURATED SOLUTION

Time, days	0	5	12	23	28	36
Inulin per 100 cc. of soln., g.	5.83	3.97	2.18	1.65	1.49	1.34

Summary

The solubility of dahlia inulin differs considerably from that of chicory inulin. Each of the two inulins exists in two modifications having different degrees of solubility. One of the modifications of chicory inulin is unstable, gradually changing into the less soluble form. Solubility was measured at different temperatures and in alcoholic solutions. The presence of levulose increases the solubility of dahlia inulin, but has no effect on the solubility of chicory inulin. Soluble inulin has no effect on the solubility of either dahlia or chicory inulin. Inulin is slowly deposited from its supersaturated solutions until normal solubility is reached.

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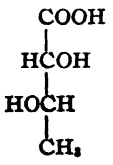
The C_4-Saccharinic Acids. VII. The Preparation and Resolution of *dl-threo*-1,2-Dihydroxybutyric Acid[1]

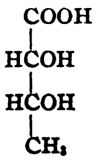
BY J. W. E. GLATTFELD AND JOHN W. CHITTUM

There are two theoretically possible *dl*-1,2-dihydroxybutyric acids. Both of these have recently been prepared in pure form and studied quite thoroughly.[2] One melts at 74–75° and the other at 81.5°. In still more recent work in this Laboratory[3] it has been shown that the acid of lower melting point probably has the *trans* configuration and the one of higher melting point the *cis* configuration. Braun has suggested the prefix *threo* for the *trans* acid and *erythro* for the *cis* acid. These suggestions are adopted in this paper.



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HOCH} \\ | \\ \mathrm{CH_3} \end{array}$$

dl-threo-1,2-Dihydroxy-butyric acid, m. p. 74–75°



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{CH_3} \end{array}$$

dl-erythro-1,2-Dihydroxy-butyric acid, m. p. 81.5°

It is with the *dl-threo*-acid that this paper is concerned.

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(1) This article is largely from a dissertation presented by John W. Chittum in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

(2) Glattfeld and Woodruff, THIS JOURNAL, 49, 2309 (1927).

(3) Géza Braun, *ibid.*, 51, 228 (1929).

dl-threo-1,2-Dihydroxybutyric acid was prepared by Glattfeld and Woodruff by the oxidation of crotonic acid of m. p. 72° by means of potassium chlorate in the presence of osmium tetroxide and also by means of barium permanganate. The work with potassium chlorate was repeated and the results verified but an additional fact was established that may affect seriously the yield of acid if ignored, namely, the fact that the free *dl-threo*-acid forms a compound with its own potassium salt that is comparatively insoluble in cold alcohol. The formation of this compound was observed about the same time by Braun, who analyzed it[4] and showed it to have the composition corresponding to the formula $C_4H_8O_4 \cdot C_4H_7O_4K$. We substantiated this formula further by preparing the compound from equal parts of the free acid and its potassium salt.

The chlorate method of preparation was greatly improved upon by Braun who used silver chlorate instead of potassium chlorate and thus avoided the complication due to the formation of the potassium double compound. We found this method to be by far the best one for the preparation of this acid.

The only report of work on the resolution of the *dl-threo*-acid is by Morrell and Hanson.[5] These workers prepared the acid by the oxidation of solid crotonic acid with barium permanganate. They failed to resolve the acid by the use of quinine, cinchonine, strychnine, morphine and brucine but reported partial success with quinidine. By the use of the last named alkaloid they obtained a *levo* acid whose specific rotation they report as −13.51°. Calculation of the specific rotation from the data they record, however, gives −19.08° instead of −13.51° and thus the correct rotation is left in doubt. Moreover, the free *dextro* acid was not obtained.

In the experimental work reported below the resolution of the acid was accomplished by means of brucine as well as quinidine. Both *dextro* and *levo* components were obtained in pure form in each case and found to have specific rotations of about −15.1 and +15.1° in the experiments in which brucine was used and −15.5 and +15.45° in those in which quinidine was used. The resolutions with the two alkaloids were made by different workers and at different times and the small differences in results are probably due to experimental error. It is probable that the true specific rotations at 20° lie somewhere between the figures recorded above.

Experimental Part

The Double Compound, $C_4H_8O_4 \cdot C_4H_7O_4K$.—As the silver chlorate procedure has been found to be much more satisfactory than the one in which potassium chlorate is used, the latter will be discussed here only to record our work with the double compound formed by the acid and its potassium salt.

To a solution of 50 g. of crotonic acid (m. p. 72°) in 1 liter of water was added 95 g. of potassium chlorate and 20 cc. of a 0.3% solution of osmium tetroxide. After having stood for one week, the solution no longer decolorized bromine water. After extraction with benzene, it was concentrated at 60° at reduced pressure until the crystals which appeared caused bumping. The crystals (49 g. of practically pure potassium chlorate) were removed and the filtrate evaporated to dryness at reduced pressure and 60°. The residual sirup was dissolved in 150 cc. of absolute ethyl alcohol and the insoluble material separated by filtration while hot. As the filtrate cooled it deposited crystals. It was, therefore, thoroughly chilled and yielded 40 g. of white solid. This product was purified by solution in hot absolute alcohol, addition of ethyl acetate to turbidity, removal of turbidity with a little alcohol, and cooling of the solution. The crystals then deposited melted at 101–103° but still contained some chloride and chlorate.

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[4] Braun, THIS JOURNAL, 51, 244 (1929).

[5] Morrell and Hanson, *J. Chem. Soc.*, 85, 197 (1904).

These crystals were very soluble in water, almost insoluble in cold absolute alcohol, and insoluble in ethyl acetate and ether. The water solution was distinctly acid. With phenylhydrazine the substance gave a crystalline derivative of m. p. 132° and with brucine a salt of m. p. 229.5°. Authentic samples of the phenylhydrazide and the brucine salt of the *dl-threo*-acid melted at 130–131° and 232–234°, respectively, and mixtures of the corresponding compounds from the two sources melted over the same ranges as the pure individuals. These facts leave little doubt that the solid under discussion contained *dl-threo*-acid.

All doubt as to the identity of the compound was finally dispelled by its synthesis from its two constituents. Ten grams of crystalline *dl-threo*-acid was dissolved in 80 cc. of water. Half of this solution was carefully neutralized with a dilute solution of potassium hydroxide. The neutralized solution was then mixed with the untreated portion of the acid solution and the mixture evaporated to dryness at reduced pressure, water-bath at 70°. The sirup was dissolved in 25 cc. of hot absolute alcohol. The alcoholic solution yielded, on cooling, a quantity of fine white crystals which were collected on a filter, washed with ether and dried; yield 7.9 g., melting range 104–107°. A second crop of crystals was obtained by concentration at reduced pressure; weight 1.8 g.; melting range 95–106°. The total yield was, therefore, 9.7 g. or 83.6% of the theoretical amount.

The Silver Chlorate Method of Preparation.—Our procedure was practically that of Braun's second method,[6] except that we did not carry out the oxidation at zero degrees but at room temperature. To a solution of 100 g. of crotonic acid (m. p. 72°) in 5 liters of water which contained 0.25 g. of osmium tetroxide, was added 2.5 g. of silver chlorate twice daily until the reaction was complete (solution no longer turned brown even after standing for twenty-four hours); total amount of silver chlorate added 96 g., time required, three weeks. The solution was stored in the dark during the preparation. The silver chloride was then separated by filtration and washed with water, after which it was washed immediately with hydrochloric acid in order to destroy any silver oxalate that might have been present as this compound is explosive when dry. The water solution was extracted three times with 300 cc. of benzene to remove the osmium tetroxide and distilled to dryness at reduced pressure (bath at 60°). The residue was treated with sufficient ethyl acetate to dissolve the gum and the solution cooled. A small amount of material did not dissolve. Fresh ethyl acetate was then added to the solution until no more cloudiness was produced by further addition. The filtered solution was dried with sodium sulfate and then concentrated at reduced pressure to a small volume (150–200 cc.), transferred to a small flask and cooled in ice water for an hour. Crystallization was induced by scratching the walls of the flask with a glass rod. A crop of crystals which, after drying in a vacuum desiccator, weighed 80.5 g. was removed. The mother liquor was concentrated and two further crops of 7.5 g. and 4 g. obtained; total 92 g. of dry crystalline acid of m. p. 73.5–75.5° or 66%.

A repetition of this experiment with 80 g. of crotonic acid yielded 78 g. of crystalline acid or 70%.

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(6) Braun, THIS JOURNAL, **51**, 245 (1929).

The acid thus obtained is of a very much higher degree of purity than when either potassium or barium chlorate is used. The reaction proceeds more slowly than when either of these reagents is used but, once it is finished, the rest of the procedure is shorter and easier to carry out, and the yields by the silver chlorate method are much higher.

If it is desired to obtain acid of the highest purity, the crystals obtained as outlined above may be dissolved in two parts of ethyl acetate at 60°, followed by chilling of the solution to 0°. The crystals are washed on the suction filter first with a little cold ethyl acetate, then with ether, and dried in a vacuum desiccator over phosphorus pentoxide and paraffin. Crystals obtained by the barium chlorate method and purified in this manner melted at 73–74° and titrated correctly.

Neither the *dl*-acid nor either of the active acids is at all hygroscopic when pure. We have exposed all three to the laboratory atmosphere for days with no evidence of absorption of moisture.

Resolution of the Acid with Brucine.—Contrary to the experience of Morrell and Hanson, we found brucine to be an excellent resolving agent when water is used as the solvent.

The brucine salt was made in the usual way.[7] A mixture of twenty-five grams of recrystallized *dl-threo*-acid (m. p. 73–74°) in 800 cc. of water and 85 g. of anhydrous brucine was kept on the boiling water-bath until the solution was permanently alkaline (several hours). The solution was cooled, extracted twice with 100-cc. portions of benzene, and distilled to dryness at reduced pressure (water-bath at 70°); wt. of residue, 127 g. This was dissolved in 150 cc. of hot water, the solution cooled and allowed to stand first at room temperature for two hours and then for one hour in an ice-bath. The solid was then collected on a suction filter, pressed dry and kept in an oven at 70–75° until constant in weight; wt. 43.5 g. The mother liquor from Crop I was evaporated to dryness at reduced pressure as before. The residue, which weighed 60 g., was crystallized from 1 part of water. This process was repeated until four crops of crystals had been obtained. The residue from the mother liquor from Crop IV weighed 12 g. The solvent was changed at this point; the material was crystallized from 12 cc. of 50% ethyl alcohol. This yielded 2.8 g. of dry salt, Crop V. The residue from the filtrate from Crop V weighed 6.0 g. It was crystallized from 6 cc. of 50% ethyl alcohol and yielded 1.3 g. of dry material.

Five such experiments were made in each of which 25 g. of the *dl*-acid was used. Six crops of crystals were obtained in each case. The specific rotations of these (sodium light) are recorded below.

Experiment	Crop I	Crop II	Crop III	Crop IV	Crop V	Crop VI
A	−32.5	−24.5	−21.0	Lost	−21.8	−22.5
B	−33.5	−21.2	−21.3	−22.2	−20.5	−22.0
C	−32.9	−21.2	−20.6	−21.9	−21.0	−18.6
D	Lost	−21.7	−24.5	−23.7	−21.5	−23.0
E	−32.8	−21.4	−21.0	−23.0	−21.2	−19.6

It is apparent from these data that a partial resolution had been accomplished. Each Crop I was now recrystallized six times from water and from the results of these recrystallizations it is concluded that the pure anhydrous brucine salt of the levo acid has a specific rotation in water solution between −34.4° and −35.6°.

Preparation of the Levo Acid from the Brucine Salt.—To a solution of 40.5 g. of recrystallized brucine salt (−34.4 to −34.6°) in 200 cc. of water was added a hot solution of 12.5 g. of hydrated barium hydroxide in 200 cc. of water. The mixture was cooled, the brucine removed and the filtrate extracted five times with 75-cc. portions of benzene. The barium was exactly precipitated with sulfuric acid, the barium sulfate removed and the filtrate evaporated to dryness at reduced pressure. The residual sirup weighed 9 g. Solution in a large volume (200–300 cc.) of ethyl acetate, filtration to remove gummy precipitate, and distillation of filtrate to dryness, gave 6 g. of gum which crystallized when seeded with racemic acid. The crystals were brought on a filter, washed with a little cold ethyl acetate and dried; m. p. 73.5–75°, $[\alpha]_D$ −15.0°.

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[7] Glattfeld and Hanke, This Journal, 40, 976 (1918).

A second portion of 75.2 g. of brucine salt (−35.1 to −35.7°) was treated in the manner outlined above. The rotation of the acid after three recrystallizations from ethyl acetate was −15.1°.

Preparation of the Dextro Acid from the Brucine Salt.—For the preparation of the dextro acid, various crops of brucine salt, −20.7 to −22.7°, were combined; weight 134.2 g. This salt was hydrolyzed in the manner outlined above for the levo acid and yielded 27 g. of crude crystalline acid; +11.3°. Fourteen grams of this material was subjected to five successive crystallizations from two parts of ethyl acetate and the specific rotation of the final product was found to be +15.1°.

Resolution of the Acid with Quinidine.—The work of Morrell and Hanson with quinidine was repeated. To a solution of 20 g. of the acid, m. p. 73.5–74.5°, in 400 cc. of hot water, quinidine was added until the solution was neutral (59 g. of alkaloid needed). The hot solution was filtered and deposited a crop of crystals which weighed 37.3 g. after three days in a vacuum desiccator over sulfuric acid; m. p. 117–117.5°; $[\alpha]_D$ +142.7°. Morrell and Hanson give 113–114° and +143.46° for the corresponding crop of crystals. They report the specific rotation as +142.2° after the material had been recrystallized six times. Our quinidine salt was recrystallized five times and then had a specific rotation of +147.5°. Further work with this salt showed it to be so much less soluble in water than the salt of the dextro acid that an almost complete separation of the two acids was found to be possible by the use of quinidine. The results recorded below support this statement.

A mixture of 60 g. of *dl* acid, m. p. 73.5–75°, in 2.5 liters of water, and 180 g. of quinidine was kept on the boiling water-bath for a half hour, cooled, filtered (2 g. of quinidine recovered) and the filtrate extracted three times with 500-cc. portions of ether. The solution was then concentrated at reduced pressure and brought to a weight of 1455 g. (1 part salt in 5 parts water), heated until all the solid was again in solution, then cooled rapidly and allowed to stand overnight. The crystals were then removed and dried in a vacuum desiccator over sulfuric acid for three days; wt. 90.3 g., $[\alpha]_D$ +147.5°; m. p. 116–122°.

It was found that it is the hydrated form of this salt which melts at 116–122° and that the m. p. must be taken rapidly to get this low value. If it is taken slowly, a very indefinite melting is observed with the last of the material liquefying at 159–162°. If the air-dry salt is extracted with boiling anhydrous ether (as is often done to avoid possible contamination with free alkaloid) it always melts at the higher value.

The filtrate from the first crop of crystals was concentrated and adjusted as before until it weighed 1395 g., cooled, seeded with crop 1 and allowed to stand for three days. The second crop was then removed; wt. 14 g., $[\alpha]_D$ +147.5°; m. p. (after ether treatment) 159–162°. A third crop of crystals was obtained by concentration of the filtrate to 1175 g. Crystals came very slowly this time even when the solution was stored for several days in the ice box; wt. crop 3, 6.8 g., $[\alpha]_D$ +149.5°; m. p. (after ether treatment) 159–162°.

The three crops of crystals were combined, wt. 106 g. (some material lost in tests of various sorts) and the filtrates and washings concentrated to dryness at reduced pressure, wt. residue 126 g. The acids were now set free from these two lots of material.

Active Acids from Quinidine Salts.—The two lots of salts were separately treated in 4–5 liters of hot water with an excess of barium hydroxide in hot solution, the mixtures cooled, the quinidine separated by filtration, the filtrates extracted with ether, the barium exactly removed as sulfate and the filtrates distilled to dryness at reduced pressure with water-bath finally at 100°; wts. of residues 24.5 g. from the crystalline salts, and 31 g. from the non-crystalline salts. Small samples of each were removed and the specific rotation determined. Then the residues were recrystallized from one and one-half parts of ethyl acetate and the specific rotation of the crystals obtained, again determined. This process was repeated five times with both levo and dextro acids. The results are recorded in the following table:

	Levo acid			Dextro acid		
	Weight, g.	$[\alpha]_D$		Weight, g.	$[\alpha]_D$	
Residue	24.5	−13.55°		31	+12.17°	
Crop 1	9	−15.9°	Av. −15.5	15	+13.4°	
Crop 2	7	−15.6°		11	+15.4°	Av. +15.45
Crop 3	5.5	−15.2°		10	+15.5°	
Crop 4	4	−15.1°		8	+15.1°	
Crop 5	2	−15.7°		6.5	+15.8°	

Summary

It has been shown that in the preparation of *dl-threo*-1,2-dihydroxybutyric acid by the method of Glattfeld and Woodruff (oxidation of solid crotonic acid by means of potassium chlorate) a compound of formula $C_4H_8O_4 \cdot C_4H_7O_4K$ is formed which may lower the yield of acid. The method of Géza Braun (use of silver chlorate instead of potassium chlorate) avoids this difficulty and was found to be much superior.

The acid prepared by Braun's method was successfully and completely resolved with brucine and with quinidine. The specific rotations of the acids obtained when brucine was used were −15.0 and +15.1°, and when quinidine was used −15.5 and +15.45°. It is probable that the correct rotations at 20° lie somewhere between these two figures.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Reaction of Nitrogen Trichloride with Grignard Reagents

BY GEORGE H. COLEMAN, MARION A. BUCHANAN AND W. L. PAXSON

In a study of the reaction of boron trichloride and other chlorides with organomagnesium halides Strecker[1] tried the reaction of nitrogen trichloride with ethylmagnesium bromide and phenylmagnesium bromide and reported that only ammonium salts were formed. Le Fèvre[2] later obtained chlorobenzene but no amines from the reaction of phenylmagnesium bromide with nitrogen trichloride.

It has been shown in this Laboratory that monochloroamine[3] reacts with organomagnesium halides to form primary amines and ammonia. The similarity of nitrogen trichloride to monochloroamine suggested that it might also react with Grignard reagents to form amines.

The yields of amines obtained from Grignard reagents and monochloroamine vary greatly with the halogen present in the reagent, decreasing in the order, chlorine, bromine, iodine. It seemed probable, therefore, that if amines were formed in the nitrogen trichloride experiments mentioned they were formed in only small amounts and were overlooked in the relatively large amounts of ammonia. The results of the work here reported indicate that this was the case.

The reaction of nitrogen trichloride with Grignard reagents is similar to that of monochloroamine and was carried out in much the same manner. Primary amines, secondary amines, ammonia and nitrogen are the principal products. The reactions for the formation of the amines and ammonia may be represented by equations similar to those given for the reaction with monochloroamine. The results obtained with fifteen Grignard reagents are given in Table I. The percentage yields are based upon the nitrogen trichloride since the Grignard reagents were always used in excess.

The yields of primary amines are several times as large as the yields of secondary amines. This was to be expected in the light of the results of the reaction of alkyldichloroamines[4] with Grignard reagents in which the yields of secondary amines were never more than twenty-five per cent. In the products of only one reaction, that with benzylmagnesium chloride, was a tertiary amine definitely identified.

A variation in the yields of amines similar to that with monochloroamine with reagents prepared from chlorides, bromides, and iodides was observed in this work. It is probable that this variation is characteristic of the reaction of Grignard reagents with halogen derivatives of nitrogen com-

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(1) Strecker, *Ber.*, **43**, 1131 (1910).

(2) Le Fèvre, *J. Chem. Soc.*, 1745 (1932).

(3) Coleman and Hauser, THIS JOURNAL, **50**, 1193 (1928); Coleman and Yager, *ibid.*, **51**, 567 (1929).

(4) Coleman, *ibid.*, **55**, 3001 (1933).

TABLE I

PERCENTAGE YIELDS OF PRIMARY AND SECONDARY AMINES AND AMMONIA FROM NITROGEN TRICHLORIDE AND GRIGNARD REAGENTS

	X = Cl			X = Br			X = I		
Reagent	RNH_2	R_2NH	NH_3	RNH_2	R_2NH	NH_3	RNH_2	R_2NH	NH_3
C_2H_5MgX	29	6	22	16	2	30	3	1	26
n-C_4H_9MgX[a]	37	5	15	21	2	20	4	1	31
n-$C_5H_{11}MgX$	21	5	21						
i-C_3H_7MgX	23	2	23						
s-C_4H_9MgX	23	3	26	10	1	31	3	1	26
t-C_4H_9MgX	30	2	15						
C_6H_5MgX	4	1	38						
$C_6H_5CH_2MgX$[b]	32	7	8						
$C_6H_5CH_2CH_2MgX$	20	2	27						

[a] The nitrogen gas given off during the reaction with *n*-butylmagnesium chloride was determined and found to correspond to 37% of the nitrogen trichloride used.

[b] In this reaction a trace of tribenzylamine was formed.

pounds in which the halogen is attached directly to nitrogen. The yields of amines are, in general, considerably smaller than the yields from monochloroamine. The formation of large amounts of nitrogen observed in this work is not characteristic of the reaction with monochloroamine.

A number of methods for the analysis of nitrogen trichloride have been used by the different investigators who have worked with this compound. Some have used more than one method. Noyes,[5] for example, has compared the hydrochloric acid method for nitrogen with the sodium sulfite method and reports that the former gives slightly higher results. There has been, however, no systematic comparison of several methods for both nitrogen and chlorine to determine their relative accuracy.

Both for the purpose of determining the best method for use in this work and because the same or very similar methods are used in the analysis of many halogen derivatives of nitrogen compounds in which halogen is attached directly to nitrogen, such a comparison has been made, the results of which are given in the experimental part.

Experimental

Preparation of Nitrogen Trichloride.—The solutions of nitrogen trichloride were prepared by a slight modification of the method previously described.[6] For the reactions with Grignard reagents ether was used as the solvent. For the comparison of methods of analysis carbon tetrachloride was the solvent. With ether as the solvent it was necessary on account of its volatility and solubility to add a little larger volume than that desired in the final solution. The reaction flask was also fitted with a reflux condenser. The tube through which the chlorine was introduced extended just to the interface between the aqueous and ethereal layers. A normal solution of ammonium nitrate was the source of nitrogen. Chlorine was either prepared as needed from sodium dichromate and hydrochloric acid or drawn from a cylinder.

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(5) Noyes, THIS JOURNAL, **42**, 2173 (1920).

(6) Coleman with Noyes, *ibid.*, **43**, 2211 (1921); Coleman and Howells, *ibid.*, **45**, 3084 (1923).

Reaction of Nitrogen Trichloride with Grignard Reagents.—Ethereal solutions of nitrogen trichloride containing about 0.10 mole in 300 cc. of solution were added slowly to the Grignard reagents containing about 0.40 mole in 400 cc. of solution. The reaction was very similar to that of monochloroamine or the alkylchloroamines with Grignard reagents. The procedure followed in carrying out the reaction and separating the products was the same as that used with alkylchloroamines.[4]

Comparison of Methods of Analysis of Nitrogen Trichloride.—In this comparison five methods were studied. The sodium sulfite method of Bray and Dowell[7] was followed very closely. The slightly modified[8] hydrochloric acid method of Noyes[8] was used for nitrogen together with the determination of chlorine in the same sample by passing the liberated chlorine into potassium iodide solution. The sulfur dioxide method of Chapin,[9] slightly modified, was used for both nitrogen and chlorine. Assuming that sodium bisulfite might combine the advantages of both sodium sulfite and sulfur dioxide, a method using this reagent was included. The method in which nitrogen trichloride is added directly to potassium iodide solution was tried but was found to give results so variable that they were not included.

In Table II are shown the results of a typical series of analyses in triplicate for nitrogen and chlorine by each of the four methods.

TABLE II

ANALYSIS OF A SOLUTION OF NITROGEN TRICHLORIDE BY FOUR METHODS

Results are expressed in milligram atoms per cubic centimeter of solution

Reagents	Nitrogen, mg. atoms	Chlorine, mg. atoms	Ratio Cl/N	Reagents	Nitrogen, mg. atoms	Chlorine, mg. atoms	Ratio Cl/N
HCl and KI	0.413	1.260	3.05	SO_2	0.418	1.259	3.02
	.415	1.264	3.04		.420	1.257	3.00
	.410	1.258	3.06		.417	1.262	3.00
Na_2SO_3	.404	1.261	3.09	$NaHSO_3$	.417	1.260	3.02
	.405	1.263	3.11		.417	1.265	3.03
	.406	1.263	3.09		.417	1.258	3.01

The fact that the chlorine to nitrogen ratio is not exactly three in each case is not necessarily significant. Solutions prepared as described sometimes have, shortly after preparation, a chlorine to nitrogen ratio which is slightly less than three. This usually increases due to slow decomposition and loss of nitrogen.

It is evident that all four methods are fairly satisfactory. The values for chlorine are practically the same throughout. The values for nitrogen by the sodium sulfite method are slightly lower than those obtained by the other three methods.

Summary

Nitrogen trichloride reacts with Grignard reagents to form primary amines, secondary amines, ammonia and nitrogen. In at least one reaction, that with benzylmagnesium chloride, a trace of a tertiary amine is formed.

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(7) Bray and Dowell, THIS JOURNAL, **39**, 896 (1917).

(8) Coleman and Craig, *ibid.*, **50**, 1816 (1928); Noyes, *ibid.*, **42**, 2173 (1920); Noyes, *ibid.*, **50**, 2902 (1928).

(9) Chapin, *ibid.*, **51**, 2112 (1929).

The yields of primary amines are several times as large as the yields of secondary amines. The total yield of amines in any reaction is however less than the yield of primary amine in the reaction of monochloroamine with the same reagent.

IOWA CITY, IOWA
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The Course of Addition of Sodium Enol Alkylmalonic Esters to Phenyl Isothiocyanate

BY JOHN ROSS

It has been shown that sodium enol malonic ester adds readily to phenyl isothiocyanate to give the sodium enolate of the monothioanilide of methane tricarboxylic ester.[1] Ruhemann[2] found that on treating this sodium enolate with benzyl chloride, a thiobenzyl ether was obtained, and he considered that this fact supported the original formulation of the addition reaction in which Na- and -CH(COOEt)$_2$ were written as addendum components. According to this view of the reaction mechanism, Ruhemann expected that the sodium enolates of monoalkyl malonic esters would also add to phenyl isothiocyanate, but he found that benzylmalonic ester was recovered unchanged from the reaction between sodium enol benzylmalonate and phenyl isothiocyanate in alcoholic solution, the phenyl isothiocyanate being converted completely into the enolate of phenyl thiourethan by the addition of sodium ethoxide.

Worrall[3] states that by the action of sodium enol α-ethylacetoacetic ester on phenyl isothiocyanate he obtained an addition product, but he did not prove the composition of this compound.

Phenyl isocyanate readily combines with enolates such as sodium enol malonic ester, but addition of sodium enol alkylmalonic esters to phenyl isocyanate does not take place, and the phenyl isocyanate is polymerized under the conditions of the reaction.[4] Phenyl isothiocyanate does not polymerize under the conditions of these reactions and for this reason its action toward compounds of sodium enol alkyl malonic ester type was examined. Moreover, since the monothioanilide of methane tricarboxylic ester gives a stable thio ether, the possibility of alkyl group migration might be expected to exhibit itself in this reaction.

In alcohol-free ether, sodium enol malonate adds to phenyl isothiocyanate to give the theoretical yield of the sodium enolate of the monothioanilide of methane tricarboxylic ester. This sodium derivative with methyl iodide gives a thiomethyl ether, but this result of alkylation is no

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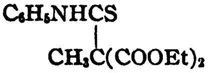
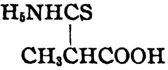
(1) Michael, *J. prakt. Chem.*, **35**, 450 (1887).
(2) Ruhemann, *J. Chem. Soc.*, **93**, 621 (1908).
(3) Worrall, THIS JOURNAL, **40**, 415 (1918).
(4) Michael, *Ber.*, **38**, 22 (1905).

evidence in itself as to the position of the sodium in the sodium enolate formed in the addition reaction. By the action of sodium enol methylmalonate upon phenyl isothiocyanate in dry ether there was obtained a 12–15% yield of the sodium enolate of the simple addition product (I), a 20% yield of phenyl thiourethan and there was recovered about 60% of unchanged reactants (methylmalonic ester and phenyl isothiocyanate). When the methyl ester of methylmalonic acid was used under similar conditions, no addition compound was formed, the products consisting of a small amount of methylphenyl thiourethan and unchanged reactants (80%). The addition of sodium enol methylmalonic methyl ester to phenyl isothiocyanate in methyl alcohol gave only methylphenyl thiourethan and the methylmalonic methyl ester was recovered unchanged. Attempted addition using a fraction of the molecular equivalent of sodium enolate in dry ether was likewise unsuccessful.



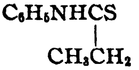
$$\begin{array}{l} C_6H_5NHCS \\ \quad\ | \\ CH_3C(COOEt)_2 \end{array}$$

I



$$\begin{array}{l} C_6H_5NHCS \\ \quad\ | \\ CH_3CHCOOH \end{array}$$

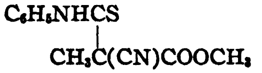
II



$$\begin{array}{l} C_6H_5NHCS \\ \quad\ | \\ CH_3CH_2 \end{array}$$

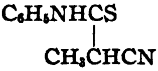
III

Sodium enol cyanacetic methyl ester in methyl alcohol with phenyl isothiocyanate gave the theoretical yield of the sodium enolate of the monothioanilide of cyanomalonic methyl ester. In contrast to this result sodium enol α-cyanopropionic methyl ester with phenyl isothiocyanate in methyl alcohol gave a small amount (6–10%) of the sodium enolate of the monothioanilide of α-cyanopropionic acid (V), phenylmethyl urethan and some unchanged α-cyanopropionic ester was recovered. The monothioanilide of α-cyanopropionic acid was apparently derived from the simple addition product, namely, the monothioanilide of α-cyano-α-carbomethoxypropionic ester (IV) by the loss of the —$COOCH_3$ group.



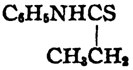
$$\begin{array}{l} C_6H_5NHCS \\ \quad\ | \\ CH_3C(CN)COOCH_3 \end{array}$$

IV



$$\begin{array}{l} C_6H_5NHCS \\ \quad\ | \\ CH_3CHCN \end{array}$$

V



$$\begin{array}{l} C_6H_5NHCS \\ \quad\ | \\ CH_3CH_2 \end{array}$$

In dry ether no addition product was formed from sodium enol α-cyanopropionic methyl ester and phenyl isothiocyanate, a small amount of phenylmethyl thiourethan being formed and unchanged reactants (80% of α-cyanopropionic methyl ester and phenyl isothiocyanate) being recovered.

The structure of the addition compounds was proved by saponification and elimination of the carboxyl groups to form thiopropionic anilide. The thiomethyl ether of the monothioanilide of methane tricarboxylic ester is stable toward sodium ethoxide in the cold, so that had this ether been formed in the reaction, it should have been possible to detect its presence. Therefore there is no evidence in these reactions with phenyl isothiocyanate of any migration of the alkyl group.

The whole subject of the mechanism of malonic ester addition reactions has been discussed recently[5,6] and it is necessary to consider the results described in this paper with reference to the views previously put forward.

Clearly, the simple ionic mechanism of the addition reaction would require yields of the same order of magnitude for the addition of sodium enol malonic as for sodium enol alkylmalonic esters. The question of ionization in this type of reaction with phenyl isocyanate has been discussed by Michael[4] and Dieckmann and others.[7] It has been shown that the yields of addition products are 100% for the addition of sodium enol malonates and less than 15% in the case of addition of sodium enol alkyl malonates. This disparity certainly does not support the ionic viewpoint and would appear to indicate a difference in the mechanism of addition of the two types of sodium enolates.

It has previously been stated[5] that sodium enol malonate adds by virtue of migration of the hydrogen atom so that addendum components are H and $-C(COOEt)=C(ONa,OEt)$. The results described in this paper are in agreement with the general ease and velocity with which such a reaction would be expected to proceed.

It has also been shown[5] that addition of malonic and alkylmalonic esters can be achieved by the aid of small amounts of alkaline reagents (*e. g.*, sodium ethoxide, nitrogen bases, caustic soda). When either of the reactants or the product is a relatively strong acid (*i. e.*, forms a relatively neutral sodium enolate), this catalytic reaction stops when the sodium or the base is neutralized.[8]

In the absence of conclusive evidence as to the migration of the alkyl group and the apparent small tendency of sodium enol alkyl malonate to combine directly with phenyl isothiocyanate, the only valid conclusion would appear to be that the addition of alkyl malonic esters to phenyl isothiocyanate proceeds solely by the above catalytic method. Explanations based upon the polar or steric effect of the alkyl group in sodium enol methylmalonate are rejected because previous work has not indicated that such effects would be of sufficient magnitude to account for the above results. Moreover, such explanations involve a simple ionic mode of reaction mechanism which is not experimentally supported.

In the preparation of sodium enol malonic esters it is almost impossible to exclude completely the presence or production of alcohol (as sodium ethoxide). In the reaction between methylmalonic ester and phenyl isothiocyanate the catalytic chain of addition is rapidly stopped, (a) because the sodium ethoxide reacts with the phenyl isothiocyanate to give the sodium enolate of the thiourethan and also (b) because the enolized

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(5) Michael and Ross, THIS JOURNAL, **52**, 4598 (1930); **53**, 1150 (1931); **55**, 1632 (1933).

(6) Holden and Lapworth, *J. Chem. Soc.*, 2368 (1931).

(7) Dieckmann, Hoppe and Stein, *Ber.*, **37**, 4627 (1904).

(8) *Cf.* the addition of nitromethane to unsaturated esters. Kohler, THIS JOURNAL, **38**, 889 (1916); Kohler and Engelbrecht, *ibid.*, **41**, 764 (1919).

primary addition product is a relatively strong acid and forms an unreactive neutral sodium derivative. The phenyl isothiocyanate and sodium enol methylmalonate remain together in dry ether (in the presence of small amounts of the sodium enolates of phenyl thiourethan and monothioanilide of ethane tricarboxylic ester) and no further reaction takes place. In this way the formation of a small amount of addition product and the non-production of a large yield can be explained.

Experimental

Addition of Sodium Enol Malonate to Phenyl Isothiocyanate.—A suspension of sodium enol malonate in dry ether was prepared by the addition of 16 g. of malonic ester to 2.3 g. of pulverized sodium, and 13.5 g. of phenyl isothiocyanate in dilute ether solution was added. After standing for twenty-four hours the sodium derivative was rapidly filtered off and freed from ether in a vacuum desiccator; yield approximately theoretical (31.5 g.). Upon acidifying with mineral acid it gave the thioanilide of methane tricarboxylic ester, m. p. 60°.[1]

Alkylation.—To a suspension of 15 g. of the above powdered sodium enolate in dry ether, 8.0 g. of methyl iodide was added and the mixture left to stand for twenty-four hours cooled in ice water. The product was washed with water and dried. Upon removal of most of the ether and the addition of ligroin, almost the theoretical yield of the S-methyl ether was obtained. It crystallized in large flat prisms of m. p. 58°.

Anal. Calcd. for $C_{15}H_{19}O_4NS$: C, 58.25; H, 6.05; S, 10.38. Found: C, 58.42; H, 6.10; S, 10.28.

When boiled with hydrochloric acid the ether hydrolyzed, giving methyl hydrosulfide and aniline. The methyl hydrosulfide was absorbed in mercuric cyanide and identified by the crystalline compound of m. p. 175° so formed.[9] To a suspension of alcohol-free sodium ethoxide prepared from 0.8 g. of sodium a solution of 10 g. of the above S-methyl ether was added. After standing for twenty-four hours the mixture was acidified and worked up as usual. There was recovered unchanged 9.5 g. of the S-methyl ether. A trace of yellow oil was left which smelt strongly of phenyl carbylamine.

Addition of Sodium Enol Methylmalonic Ester to Phenyl Isothiocyanate.—To a suspension in ether of sodium enol methylmalonic ester prepared from 17.4 g. of methylmalonic ester and 2.3 g. of pulverized sodium, 13.5 g. of phenyl isothiocyanate was added. A faintly yellow solution was obtained. After standing at room temperature for two days, the mixture was acidified, washed with water and the ether extract dried and distilled under reduced pressure; 19 g. of a mixture of methylmalonic ester and phenyl isothiocyanate distilled over at 85–100° (3 mm.) and then the distillation was stopped. The unchanged material represented 60% of the total reactants. The residue in the flask was taken up in the minimum of ether and ligroin added until crystallization began.

Monothioanilide of ethane α,α,α-tricarboxylic ester crystallized out first in large faintly yellow prisms which were recrystallized and melted at 92°. The yield of 4.0 g. represented about 12% of the total reactants.

Anal. Calcd. for $C_{15}H_{19}O_4NS$: C, 58.25; H, 6.05; S, 10.38. Found: C, 58.36; H, 6.12; S, 10.25.

The residue in the mother liquor after removal of the above thioanilide proved to be almost entirely phenyl thiourethan. This crystallized in large flat needles, m. p. 71°. The yield was 6.0 g., approx. 20% of the total reactants.

Monothioanilide of Methylmalonic Acid.—The monothioanilide of ethane α,α,α-

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(9) S. P. Mulliken, "Identification of Organic Compounds," Vol. III, 1922, p. 216.

tricarboxylic ester dissolved immediately in a slight excess of 10% caustic potash and after standing for three days was carefully acidified with cold dilute hydrochloric acid. There was immediate evolution of carbon dioxide and an oil was precipitated which rapidly solidified. The latter proved to be the monothioanilide of methylmalonic acid. It crystallized in faintly yellow prisms and melted at 118° with the evolution of carbon dioxide.

Anal. Calcd. for $C_{10}H_{11}O_2NS$: C, 57.42; H, 5.26; S, 15.33. Found: C, 57.65; H, 5.30; S, 15.18.

Thiopropionic anilide was obtained by heating a small amount of the above monothioanilide of methylmalonic acid above its melting point. It crystallized in large cubes melting at 67° and was shown by analysis and direct comparison to be identical with a sample of thiopropionic anilide prepared through the action of magnesium ethyl iodide upon phenyl isothiocyanate.[10]

Addition of Sodium Enol Cyanoacetate (Methyl Ester) to Phenyl Isothiocyanate.—To a solution of 1.2 g. of sodium in absolute methyl alcohol 4.8 g. of cyanoacetic methyl ester was added and followed by 6.7 g. of phenyl isothiocyanate. The solution became very warm but was quickly cooled in ice water. After standing for twenty-four hours, the mixture was acidified and the monothioanilide of cyanomalonic methyl ester crystallized out and was filtered off. It was recrystallized from a mixture of methyl alcohol and ether as small prisms which melted at 135° with decomposition. The yield was almost the theoretical.

Anal. Calcd. for $C_{11}H_{10}O_2N_2S$: C, 56.41; H, 4.27; S, 13.73. Found: C, 56.65; H, 4.34; S, 13.49.

Alkylation.—To a solution 1.2 g. of sodium in 15 cc. of methyl alcohol was added 4.8 g. of cyanoacetic methyl ester and 6.7 g. of phenyl isothiocyanate in order. After standing for several hours, 8.0 g. of methyl iodide was added and the mixture stood in the cold for twenty-four hours. The product was washed with water and the ether extract dried. Upon removal of most of the ether and adding ligroin, approximately the theoretical yield of the S-methyl ether was obtained. It crystallized in large prisms, m. p. 83°.

Anal. Calcd. for $C_{12}H_{13}O_2N_2S$: C, 56.74; H, 4.83; S, 12.93. Found: C, 56.50: H, 4.95; S, 12.75.

When boiled with hydrochloric acid, the ether hydrolyzed to give methyl hydrosulfide.

Addition of Sodium Enol α-Cyanopropionic Methyl Ester to Phenyl Isothiocyanate.—To a solution of 1.2 g. of sodium in 15 cc. of methyl alcohol was added 5.7 g. of α-cyanopropionic methyl ester followed by 6.7 g. of phenyl isothiocyanate, the mixture being cooled in ice water. After standing for twenty-four hours the product was acidified and the ether extract dried. After removal of most of the ether there crystallized out approx. 1.0 g. of the monothioanilide of α-cyanopropionic acid (representing about 10% of the reactants). This was filtered off and the residue distilled under reduced pressure; 4.5 g. of unchanged α-cyanopropionic methyl ester distilled over at 75–90° (3 mm.), then the distillation was stopped. The residue (7.0 g.) solidified completely and proved to be the methyl ester of phenylthiocarbamic acid (methylphenylthiourethan), m. p. 95°.

Monothioanilide of α-cyanopropionic acid was recrystallized from a mixture of methyl alcohol and ether. It melted at 126° without decomposition.

Anal. Calcd. for $C_{10}H_{10}N_2S$: C, 63.16; H, 5.9; S, 16.87. Found: C, 63.37; H, 6.15; S, 16,78.

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(10) Sachs and Loevy, *Ber.*, 36, 587 (1903).

A solution of this monothioanilide in excess caustic potash did not hydrolyze upon standing in the cold for three days, since upon acidification the original material was recovered unchanged. Upon boiling a solution in excess caustic potash some hydrolysis with formation of aniline occurred but the main product was the potassium salt of the monothioanilide of methylmalonic acid, m. p. 118°. This upon melting gave thiopropionic anilide, m. p. 67°, which further confirmed the structure of the original addition compound.

Summary

1. Whereas the sodium enolates of malonic and cyanoacetic esters combine readily with phenyl isothiocyanate to form approximately 100% yields of the sodium enolates of the corresponding monothioanilides, the sodium enolates of methylmalonic and α-cyanopropionic esters give only very small yields (5–15%) of the simple addition products and the major portion of the reactants is unchanged.

2. A modification of the theory of the mechanism of this addition reaction is consequently necessitated and an explanation is offered.

LONDON, ENGLAND

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[CONTRIBUTION FROM INDUSTRIAL-FARM PRODUCTS DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Resin Acids of American Turpentine Gum. The Preparation of the Pimaric Acids from Pinus Palustris[1]

BY S. PALKIN AND T. H. HARRIS

The resin acids of *Pinus maritima*, the principal French gum, have been given considerable study by Vesterberg,[2] Aschan,[3] Dupont[4,5] Ruzicka[6] and others.

The acids of the American gums, *Pinus palustris* and *Pinus carribea*, from which the bulk of the world's supply of rosin and turpentine are obtained, have received less attention.[7,8]

Pinus maritima[5,9] contains two general types of isomeric acids of the empiric formula $C_{20}H_{30}O_2$—the sapinic and the pimaric acids. The sapinic, of which two have been described (α and β), have been estimated by Dupont to represent about 70% of the total acids. These are levorotatory, very susceptible to oxidation, and easily isomerized by heat and

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(1) Presented before the Cellulose Division, Washington Meeting of the American Chemical Society, March 26–31, 1933.

(2) A. Vesterberg, *Ber.*, **18**, 3331 (1885); **19**, 2167 (1886); **20**, 3248 (1887); **38**, 4125 (1905).

(3) O. Aschan, "Naphthen Verbindungen, Terpene und Campherarten," 251–319 (1929).

(4) G. Dupont, *Bull. soc. chim.*, **29**, 718 (1921).

(5) G. Dupont and Douberg, *Bull. Inst. du Pin*, **31**, 581 (1926).

(6) L. Ruzicka, *Bull. Inst. du Pin*, **59**, 112 (1929).

(7) A. W. Schorger, *Trans. Wisconsin Acad. Sci.*, **19**, 728 (1919).

(8) Fr. Balas, "Casopis Ceskoslovenskeho Lekarnictva," **7**, 320 (1927); *Chem. Zentr.*, **100**, 2530 (1929).

(9) P. Klason and J. Köhler, *J. prakt. Chem.*, **73**, 337 (1904).

mineral acids to abietic acid, and they do not form crystalline salts. The pimaric, of which two also have been prepared, one levo (β) and the other dextro-(α)-rotatory, do possess the property of forming crystalline salts, a property which has thus far served as the principal means for their isolation from the complex acid mixture.

While the actual steps involved in the preparation of the resin acids are relatively simple, their isolation in a reasonable state of purity is rendered exceedingly difficult by a number of factors including the physical character of the gum, close similarity of their properties, their instability, and their great tendency to form isomorphous crystals.

Considerable advance in the methods of preparation was made by Dupont,[4] and later by Ruzicka and Balas,[10] and by Aschan,[3] over those of the earlier investigators. But even their improved procedures when applied to *Pinus palustris* were found to lead to certain difficulties, indicating the need for a more dependable working scheme in which greater flexibility of method as applied to acid mixtures of varying composition is provided.

By extending the observations of Ruzicka, data on the behavior of the sodium salts on fractional crystallization under certain conditions of temperature, concentration and alkalinity have been worked out. These data, together with an improved technique for obtaining the original crude acids and for liberating the acids from the sodium salts, have made possible a more expeditious separation of the pimaric and the sapinic, and the α- and β-pimaric acids from one another, than by previous means.

As shown in this paper, levo-pimaric acid from *Pinus palustris* agrees well in properties with that derived from *P. maritima*, but dextro-pimaric acid from the two sources differs markedly in rotation and melting point.[11]

The *P. palustris* gum was found to contain appreciable quantities of the two pimaric acids.

Their relative proportions, as indicated by calculations from the rotation of the mixture, was about two parts of levo to one part of dextro, a ratio similar to that observed in the French gum.[5]

Experimental Part

Treatment of the "Galipot."—The thick sirupy character of the gum turpentine medium, containing the settled crystalline acids or so-called "galipot," renders the ordinary laboratory filtration apparatus and processes inapplicable. Since the task of removing the crystalline mass from this medium is in this case attended with such extraordinary difficulties and constitutes an unavoidable step in the preparation of initial mixed acids, a convenient device providing a large filtering surface is here shown in detail in Fig. 1. A small quantity of turpentine gum spread evenly over the surface of the cloth before suction is applied will serve to seal the rim and the hood. The "galipot" mass is distributed evenly over the filter cloth in a layer about 5 cm. thick, and smoothed over with a wide spatula to insure uniform suction. Where the crystalline "galipot" is relatively coarse, the filtration proceeds rapidly. The product obtained is relatively dry to the touch.

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[10] L. Ruzicka, Fr. Balas, and Fr. Vilim, *Helv. Chim. Acta*, 7, 458 (1924).

[11] The latter, unless that from *P. palustris* is found to be a new isomer, has been prepared by this means in a higher state of purity than hitherto obtained from any other source, or by other means.

Preparation of the Mixed Acids.—Two extractions of the filtered product with 80% alcohol, and one crystallization from 95% alcohol, were found adequate to provide white crystalline pimaric acids in sufficient concentration to give a crystalline ammonium salt.[12]

The white crystalline acids yielded a pearly mass of sodium salts in one crystallization, as described later.[13]

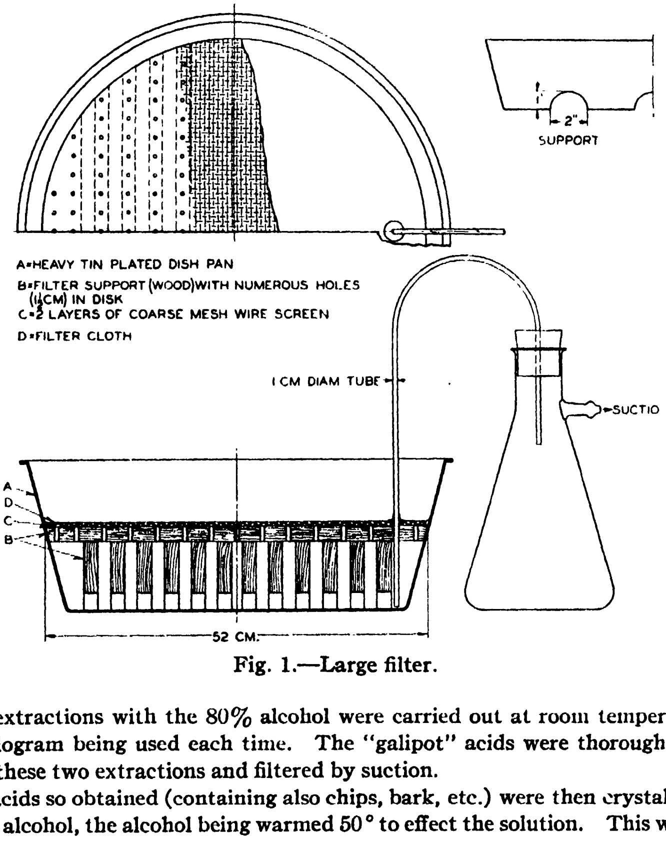
A•HEAVY TIN PLATED DISH PAN
B•FILTER SUPPORT (WOOD) WITH NUMEROUS HOLES (1½CM) IN DISK
C•2 LAYERS OF COARSE MESH WIRE SCREEN
D•FILTER CLOTH
2"
SUPPORT
1 CM DIAM TUBE
SUCTIO
A
D
C
B
52 CM.

Fig. 1.—Large filter.

The extractions with the 80% alcohol were carried out at room temperature, 500 cc. per kilogram being used each time. The "galipot" acids were thoroughly disintegrated in these two extractions and filtered by suction.

The acids so obtained (containing also chips, bark, etc.) were then crystallized once from 95% alcohol, the alcohol being warmed 50° to effect the solution. This was carried out in several stages, treating with the alcohol, filtering by suction and re-treating the residue each time with fresh alcohol to bring it into solution with a minimum of solvent. About one liter per kilogram of acids was required. The chips, bark, etc., were thus eliminated in this step.

Preparation of Crystalline Sodium Salt.—The resulting white crystalline acids were converted to the salt with warm $N/2$ sodium hydroxide (not over 50°). After cooling somewhat, the soap was precipitated with an excess of alkali (using 2 or 3 normal) more or less as described by Dupont[5] in connection with the preparation of sapinic acids. The soap was either centrifuged or filtered by suction, a filter cloth disk being used instead of paper. The resulting white soap, thus freed from oxidation products, was redissolved in a minimum quantity of warm water (about 50°), diluted with about one-half the volume of additional water and allowed to crystallize in cold storage (about 0°) for twenty-four hours. The mass of pearly crystalline pimaric acids thus obtained was either centrifuged or filtered by suction.[14]

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[12] Unless the sapinic acids have been sufficiently removed, the ammonium salt test cannot be obtained and subsequent preparation of the crystalline sodium salt is much more difficult.

[13] This preparatory treatment of the acid may be compared with the ten treatments of the pressed "galipot" found necessary by Dupont as follows: four extractions with 75% alcohol; one crystallization from 75% alcohol; three crystallizations from 80% alcohol; two crystallizations from 95% alcohol.

12.03 Kilograms of "galipot" yielded in this manner 2375 g. of crystalline sodium salt having a rotation $[\alpha]_D$ $-173°$ in terms of its corresponding acids. In another experiment 6.78 kilograms yielded 1265 g. having a rotation $[\alpha]_D$ $-164.6°$ in terms of its acids. Assuming the pure acids to have the specific rotations $[\alpha] = -279°$, and $+73°$, respectively, their relative proportions would be about 71% levo and 29% dextro in the first instance, and 68% levo and 32% dextro in the second.

Separation of Levo from Dextro Pimaric Acid.—In the following scheme for the separation of the respective pimaric acids, due consideration is given to the composition of the acid mixtures or fractions in question, rotation being the criterion as to the applicability of any particular method used. Actual composition of any given fraction (assuming only the two compounds dextro and levo pimaric acid present) may be calculated from Biot relationship as follows: $Px(\mathrm{LR}) + (1-P)x(\mathrm{DR}) = \mathrm{OR}$ where P is % levo pimaric acid; LR is specific rotation of pure levo pimaric acid; $1-P$ is % dextro pimaric acid; DR is specific rotation of pure dextro pimaric acid; OR is observed rotation of mixture.

Two general procedures were found useful for effecting a concentration of the respective acids: (1) one leading in a few steps to levo pimaric acid and applicable to pimaric acid mixtures having a rotation of $-160°$ or above. This was found more convenient and effective than fractionation from acetone as described by Ruzicka, *et al.*[10] The resin acids were liberated (quantitatively) from the sodium salts in an alcoholic solution in the cold with an equivalent of acetic acid in alcohol. (2) Another procedure leads more or less rapidly to dextro pimaric acid and is applicable to pimaric acid mixtures having rotations below $-160°$. In this method the sodium salts were subjected to a systematic crystallization in a manner similar to that described by Ruzicka,[10] modified to include fractionating advantages incident to low temperature and alkalinity. This scheme was found particularly useful for acid mixtures in which fractionation of the free acids from organic solvents was ineffective.

Method 1.—The sodium salt was dissolved in warm alcohol (about 45°), filtered by suction (paper washed with alcohol) and brought to a concentration (in a volumetric flask) of not more than 500 g. per liter. The calculated equivalent of 2 N acetic acid in alcoholic solution (using 3 or 4 cc. excess), ice cooled, was added to the previously cooled solution of sodium salt. This quantity was calculated from analytical determination of an aliquot. Crystallization (aided by stirring) soon took place. The acid filtered by suction was washed with a little ice cold 75% alcohol, and finally with water to remove all traces of acetic acid. Successive crops were obtained by progressive dilution with water. The yields and rotations of the acids so obtained are shown in Table I.

Method 2. Systematic Fractional Crystallization of the Sodium Salts.—The sodium salts were dissolved in warm water (about 50°) and diluted with cool water, the dilution depending upon the relative proportions of the respective acids as determined by the rotations of the fractions treated. In these experiments the temperature was generally not allowed to go above 50° to avoid isomerization.[6]

The progress of the fractional crystallization is indicated in the diagram (Fig. 2A). The approximate dilutions (volume of water per gram of sodium salt) are shown on the continuous lines of the chart. Except as indicated three fractions were generally ob-

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[14] In some instances repetition of this step may be desirable.

TABLE I

RESULTS OBTAINED WITH METHOD 1

Fraction No.[a]	Sodium salt taken [α][b]	Crop	Free acid obtained by direct neutralization [α]	Yield, g.
256 EFC 172 EFCD 60 CCD 25 EFC	−277 −215 −208 −215	1st	−244.3°	255
		2d	−142	60
		3d		5
75 ED	−247	1st	−268.6	27
		2d	−228.7	5
565 G	−173	1st	−219	135
		2d	−121	155
		3d	−132	30
500 G[c]	−175	1st	−251	85
		2d	−156	180
		3d	−142	40

[a] Numerical portions of fraction numbers also represent weights of fractions. [b] Spec. rotation in terms of the corresponding acid. [c] Used *N* acetic instead of 2 *N* acetic acid for neutralization.

tained, (1) at room temperature, (2) by cooling, (3) by the slow addition of alkali (about 5 *N*) until precipitation was fairly complete. These crops are indicated by the designations "r. t.", "ice," "alk.," respectively. The numerical part of the experiment numbers (just preceding the letters), represents the approximate weights of the respective fractions. Specific rotations are given directly below each experiment number. Various fractions, whose rotations were not markedly different, were combined in the usual way for further fractionation, such combinations being indicated by dotted lines connecting them. In order to render the diagram less confusing, some of the intermediate fractions are not shown.

Rotations of the various crops of sodium salt are given in terms of their corresponding acids. These we determined as follows. A weighed quantity of sodium salt (1 or 2 g.) was dissolved in a minimum quantity of alcohol and to this solution (ice cooled) was added slightly more than an equivalent of a cool alcoholic solution of 2 *N* acetic acid. (Approximately 1.2 cc. to 1.4 cc. of 2 *N* acetic acid per gram of sodium solution is generally sufficient.) A fine granular crystalline precipitate formed on stirring. Cool water was then added, drop by drop, with stirring, to effect a complete precipitation. This product, after filtration by suction and washing with water, was dried in the air and then in vacuum (at 45°). The specific rotation was generally made on a 1% alcoholic solution in a 2-decimeter tube.

This procedure was generally preferred to the liberation of the acids by way of carbon dioxide, as the latter, even when heated to 60° during precipitation, as suggested by Ruzicka, were frequently found to filter poorly.

There was virtually no isomerization by the acetic acid under the special conditions described above, as may be seen by the following determinations (Table II).

TABLE II

Experiment		1	2	3
Acids liberated with	AcOH $[\alpha]_D$	−207°	−286°	−251°
	CO_2 $[\alpha]_D$	−205°	−286°	−250°

In Experiment 3 an excess of acetic acid, over 60% more than the required equivalent, was used without any apparent isomerization.

Enrichment of the sodium salts in terms of dextro pimaric acid proceeds fairly rapidly with fractions of rotation below −100°, as may be seen from fractions 158C$_{400}$, 80CCD and 92CCD, etc. (Fig. 2A).

High concentration of dextro acid tended markedly to hydrolyze. Gradual addition of a small quantity of $N/2$ alkali to the suspension in the hot water generally cleared the solution. The progress of the purification of the levo and dextro acids may be seen from the diagram in Fig. 2B.

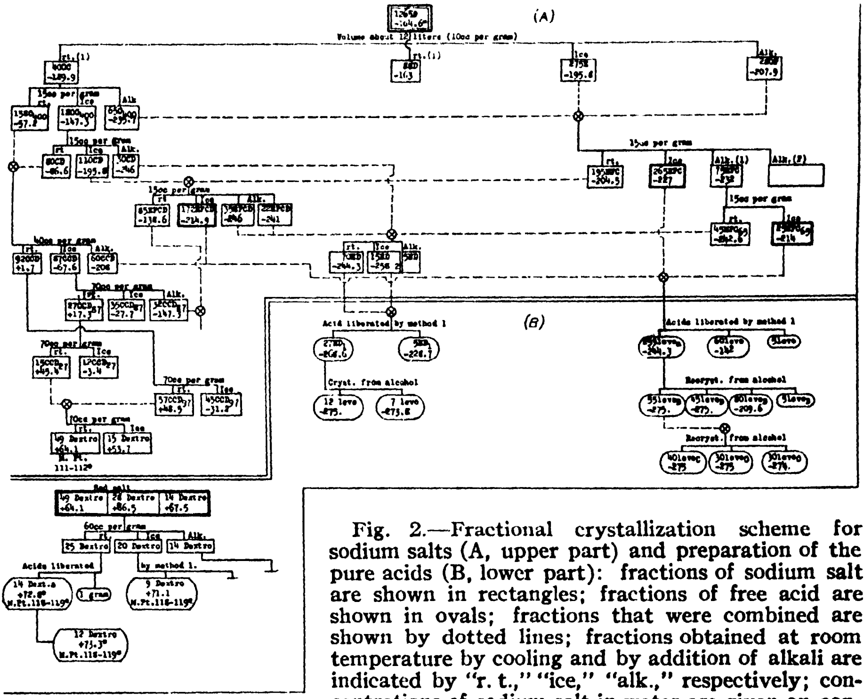

Fig. 2.—Fractional crystallization scheme for sodium salts (A, upper part) and preparation of the pure acids (B, lower part): fractions of sodium salt are shown in rectangles; fractions of free acid are shown in ovals; fractions that were combined are shown by dotted lines; fractions obtained at room temperature by cooling and by addition of alkali are indicated by "r. t.," "ice," "alk.," respectively; concentrations of sodium salt in water are given on continuous lines; numerical part (to left) of experiment numbers indicates approximate weights of fractions; specific rotation given for each fraction.

The properties of the purified levo and dextro pimaric acids obtained from longleaf pine (*Pinus palustris*) are given in Table III.

Catalytic Hydrogenation

Dihydro-levo-pimaric Acid.—Ten grams of the pure levo-pimaric acid in 85 cc. of ethyl acetate with 0.5 g. of palladium–barium sulfate catalysts,[15] absorbed 820 cc. of hydrogen in a total of two and one-half hours, 800 cc. having been absorbed in the first half hour. (Calculated volume for the dihydro compound is approximately 810 cc.)

The hydrogenated product, after removal of the catalyst and solvent, was crystallized several times from diluted alcohol (85%) as described by Ruzicka, Balas and Vilim.[10] Several isomers were apparently formed as reported by these authors, of which only one was obtained in pure form, as indicated by constancy of the melting point (m. p. 144–146°).

Dihydro-dextro-pimaric Acid.—Four grams of dextro-pimaric acid in 110 cc. of

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[15] Houben–Weyl, 2d ed., p. 500.

TABLE III

COMPARISON OF PROPERTIES OF THE PIMARIC ACIDS

Acid prepd. by		Levo pimaric acid		Dextro pimaric acid	
Balas[8]		150° $[\alpha]_D$	−280.4 (1.5% alcohol)	213°	$[\alpha]_D$ + 79.3° (0.57% alc.)
Ruzicka[9]	M. p., °C.[a]	148–151		211	$[\alpha]_D^{18}$ + 57° 0.48% abs. alc.
	Rotation	$[\alpha]_D^{17}$ (in 2% abs. alcohol)	−279.2°		$[\alpha]_D^{19}$ + 59.7° 2.9% abs. alc.
		$[\alpha]_D^{19}$ (In 5% $CHCl_3$)	−266.6		$[\alpha]_D^{17}$ + 74.7° (5% $CHCl_3$)
Dupont[4]	M. p., °C.	150–152		211–212	
	Rotation	$[\alpha]_J$	−282.4°		$[\alpha]_J$ + 63.5°
Palkin	M. p., °C.	150–152		218–219	
	Rotation	$[\alpha]_D^{20}$ $[\alpha]_J^{20}$	−274.5° −290.7° In abs. alc. 2 g. per 100 cc.		$[\alpha]_D^{20}$ + 73.3° $[\alpha]_J^{20}$ + 77° In abs. alc. 2 g. per 100 cc.
		$[\alpha]_D^{20}$ $[\alpha]_J^{20}$	−258.5° −273° In $CHCl_3$ 5 g. per 100 cc.		$[\alpha]_D^{20}$ + 87.3° $[\alpha]_J^{20}$ + 91.8° In $CHCl_3$ 5 g. per 100 cc.
Cryst. examination[b]	Crystal form	Colorless rods and plates			Colorless rods and plates
	Refr. index.	α = 1.537; β = 1.588; γ = 1.620			α = 1.556; β = 1.564; γ = 1.606

[a] Levo pimaric acid isomerizes rapidly as the melting temperature is approached. Softening takes place before substance melts to an oil. Ruzicka and Frank,[16] prepared a dextro pimaric acid, melting at 215°, by way of the dihydromethyl ester. No rotation for this is given.

[b] Crystallographic data were furnished by G. L. Keenan of the Food and Drug Administration.

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(16) L. Ruzicka and M. W. Frank, *Helv. Chim. Acta*, **15**, 1925 (1932).

ethyl acetate with 0.1 g. of palladium–barium sulfate catalysts (warmed somewhat), absorbed a total of 340 cc. of hydrogen in five hours, 270 cc. having been absorbed in the first two hours (calculated volume for dihydro compound, 325 cc.).

The reaction product after removal of the catalyst and solvent was recrystallized from ether to a constant melting point which was over 10° higher than that reported by Ruzicka and Balas[17] (m. p. 249–250°).

Anal.[18] Calcd.: C, 78.88; H, 10.60. Found: C, 78.87; H, 10.63.

The authors wish to express their appreciation to Mr. R. R. Long, of Atmore, Ala., for his coöperation in furnishing the turpentine gum.

Summary

An investigation of the pimaric acids in *P. palustris*, an improved systematic procedure for their preparation from the "gum," as well as the preparation of catalytic hydrogenation products of these acids are described.

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[17] L. Ruzicka and Fr. Balas, *Helv. Chim. Acta*, **6**, 677 (1923).

[18] These analytical data were kindly determined by J. R. Spies, Department of Chemistry, University of Maryland.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Carbon Syntheses with Malonic and Related Acids. I

BY ARTHUR MICHAEL AND JOHN ROSS

In 1879[1] it was shown that mixtures containing benzoic, or cuminic, aldehyde with phenylacetic acid and sodium acetate heated in sealed tubes gave stilbene, or propylstilbene, evidently by loss of carbon dioxide from the first-formed cinnamic acid derivatives. Subsequently,[2] this modification of the Perkin synthesis, using an acid instead of an acid anhydride, was extended to malonic acid, when, with benzoic aldehyde, cinnamic acid was obtained without use of acetate. This synthesis was not extended, as, simultaneously, Claisen and Crismer[3] found that benzalmalonic acid was formed on heating malonic acid with benzoic aldehyde in acetic acid solution, with or without acetic anhydride, and Komenos[4] that replacement of aromatic by fatty aldehydes led to the formation of aliphatic α,β,Δ-dibasic acids, or corresponding monobasic acids through loss of carbon dioxide. A large literature now exists on the use of malonic acid for the preparation of mono- and dibasic α,β,Δ-acids.[5]

Komenos[4] was unable to condense malonic acid with acetone, using acetic anhydride, but Meldrum[6] observed that addition of a little sulfuric acid to the mixture caused an immediate reaction to form the β-lactone of β-hydroxyisopropylmalonic acid. This interesting synthesis of a β-lactone has been used besides with acetone and methylmalonic acid,[7] and with several homologous ketones and malonic acid.[8] Malonic acid also has been condensed with certain aryl carbinols, yielding arylmalonic acids. Notwithstanding the extensive use of the malonic acid reaction for C-syntheses, its applicability is far from exhausted. We have undertaken a systematic investigation of the chemical behavior of this reagent and derivatives toward mono- and polycarbonyl compounds, including the enol–keto group, to determine the scope of the reaction and the relations of the products formed in the Claisen–Komenos, Meldrum and Knövenagel methods to the structures of the components of the systems.

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[1] Michael, *Am. Chem. J.*, **1**, 312 (1879).

[2] *Ibid.*, **5**, 14 (1883).

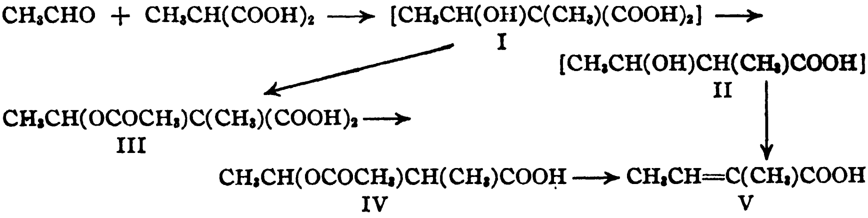
[3] Claisen and Crismer, *Ann.*, **218**, 135 (1883).

[4] Komenos, *ibid.*, 149 (1883).

[5] Beilstein, Vol. II, p. 245; Suppl., Vol. II, p. 235 (1920). Thirty researches are listed. Knövenagel used pyridine instead of acetic acid and anhydride to induce the reaction.

[6] Meldrum, *J. Chem. Soc.*, **93**, 605 (1908).

Tiglic acid has been synthesized by a number of methods, but the preparations are difficult and poor yields are obtained. A mixture of methylmalonic acid with an excess of paraldehyde, acetic anhydride and acetic acid was heated on the water-bath for several hours. There were formed tiglic acid (V) and β-acetoxy-α-methylbutyric acid (IV). The latter distilled unchanged in a vacuum, but at ordinary pressure lost acetic acid to give tiglic acid which, by these simple methods, may be obtained in a 70% yield. In this synthesis the following processes apparently occur



$CH_3CHO + CH_3CH(COOH)_2 \longrightarrow [CH_3CH(OH)C(CH_3)(COOH)_2] \longrightarrow$ I

$[CH_3CH(OH)CH(CH_3)COOH]$ II

$CH_3CH(OCOCH_3)C(CH_3)(COOH)_2 \longrightarrow$ III

$CH_3CH(OCOCH_3)CH(CH_3)COOH \longrightarrow CH_3CH{=}C(CH_3)COOH$ IV V

The stability of I toward elimination of water to form an α,β, Δ-acid is evidently due to the absence of an α-hydrogen. Compound III upon loss of carbon dioxide would form α-methyl-β-acetoxybutyric acid (IV) and tiglic acid (V) may now be formed by loss of acetic acid. This must take place with difficulty under the experimental conditions, since IV remains as a considerable proportion of total products of the reaction. It might be considered, therefore, that tiglic acid is formed solely through II by elimination of water, but this simple interpretation has been shown to be improbable.

α-Methyl-α-carboxy-β-hydroxybutyric acid (I) was prepared by a method described later in this paper. On pyrogenic decomposition at 135°, under atmospheric or reduced pressure, it gave acetaldehyde and methylmalonic acid and no appreciable amount of tiglic or α-methyl-β-hydroxybutyric acid. Therefore it seems probable that methylmalonic acid in the

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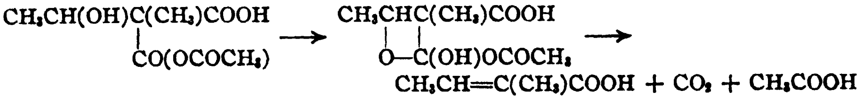
(7) Ott, *Ann.*, 401, 159 (1913).

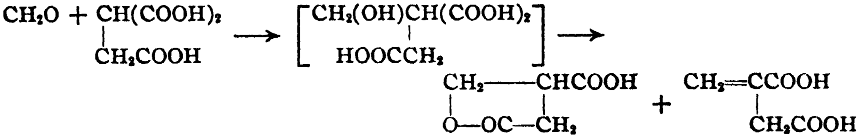
(8) Kandhiah, *J. Chem. Soc.*, 1215 (1932).

presence of paraldehyde, acetic anhydride and acetic acid follows a different course of reaction. Dimethylmalonic acid warmed with acetic anhydride gives a mixed malonic-acetic anhydride and methylmalonic acid undoubtedly reacts similarly. From this point of view, the formation of tiglic acid, besides through IV, may take place through a β-lactone derivative



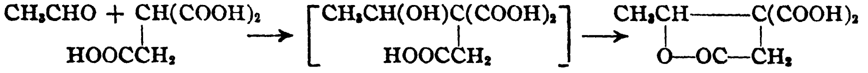
This very negative β-lactone should undergo facilely such a decomposition and all malonic acid syntheses of α,β, Δ-acids, that require the use of acetic anhydride, may proceed through a mixed acid anhydride.

In the above manner, paraformaldehyde and ethinyl tricarboxylic acid gave a good yield of paraconic acid (VI) with itaconic acid (VII) in a small proportion



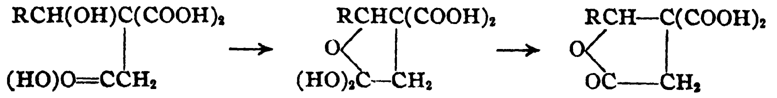
VI VII

By the same method there was produced from paraldehyde and the tricarboxylic acid in the cold an almost theoretical yield of α-carboxy-β-methylparaconic acid (IX)

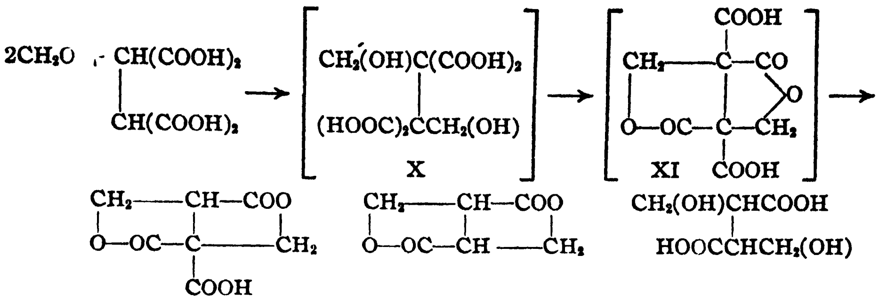


VIII IX

It is evident that when a mono-substituted malonic acid contains a carboxyl in the β-position to the dicarboxylic group, the elimination of water from the first-formed aldol derivative (*e. g.*, VIII), occurs solely, or almost entirely, by way of intramolecular esterification to form a γ-lactone

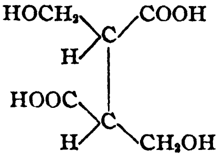


This course of reaction is again illustrated in the case of symmetrical ethane tetracarboxylic acid. That acid and paraformaldehyde, by the Claisen-Komenos method, gave with loss of carbon dioxide the γ-dilactone of dimethylolethinyl tricarboxylic acid (XII) as the main product. Upon fusion acid XII lost carbon dioxide and gave the bicyclic γ-dilactone of dimethylolsuccinic acid (XIII), the simplest possible aliphatic member of this class of dilactones. It dissolved in warm caustic soda to form the neutral sodium salt of *sym*-dimethylolsuccinic acid (XIV)

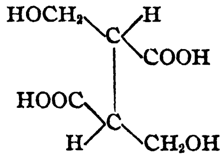


XII XIII XIV

This dihydroxy dicarboxylic acid (XIV) contains two asymmetrical carbon atoms and may exist in the racemic and meso form



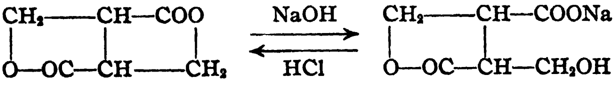
A Racemic



B Meso

From the property of γ-hydroxy acids to condense to γ-lactones, when the involved interacting groups are uniplanar, each of these stereostructures may yield a corresponding racemic and meso form of a mono-lactonic acid and a dilactone. According to Reis,[9] in the meso or "centri" form the hydrogen atoms at the asymmetrical carbon atoms are in *trans* relationship. but no chemical evidence is known to confirm this view. The dissymmetry of the hydrogen atoms should cause a decided increase of free chemical energy in the meso over the racemic stereo form This does not agree with the relative properties of the members of these groups of compounds and it is not improbable that B would pass over voluntarily into A.

The dilactone (XIII) is soluble in water and in the cold it slowly neutralizes one equivalent of alkali, with fission of one lactone ring, giving the mono-sodium salt (XV). This upon acidifying yields the original dilactone (XIII)



XIII XV

When boiled with two equivalents of caustic soda, both lactone rings are opened and approximately equal amounts of the two stereomeric sodium salts of XIV were obtained. One of the salts appeared as an octahydrate, which separated as a highly crystalline solid from the solution of the other, very soluble compound. The latter upon acidifying gave the original

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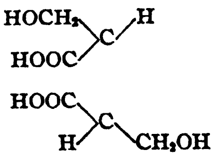
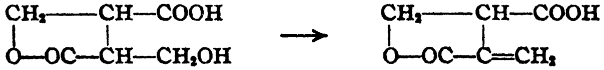
(9) Reis, *Ber.*, **59**, 1551 (1926).

dilactone. On the other hand, the less soluble sodium salt gave a monohydroxy-γ-lactonic acid (XVI).

The formation of the mono-lactonic acid from the less soluble salt can be explained only by racemization of A, when one of its COONa groups undergoes a positional interchange with the hydrogen atom attached to the same asymmetrical carbon atom. The respective methylol and the carboxyl group of the corresponding free acid are no longer in the same plane and therefore cannot undergo lactonization (C Meso). These properties of A and C are of theoretical interest as they offer a rigorous chemical proof that racemization proceeds with rearrangement at one of the asymmetrical carbon atoms. Upon treatment with a dehydrating agent the meso mono-lactonic acid XVI might be reconverted into the racemic acid (A), when it would condense to the dilactone; lose water from the methylol and carboxyl groups in *trans* position to each other, when it would undergo retrogression with elimination of carbon dioxide; or, water might be eliminated from the carbinol hydroxyl and the hydrogen atom at the same asymmetrical carbon atom, when an unsaturated lactonic acid would be formed. As the last process would occur in a β-hydroxy acid group, which always loses water very readily, it is not surprising that treatment of the meso lactonic acid XVI with acetic anhydride proceeded in this direction



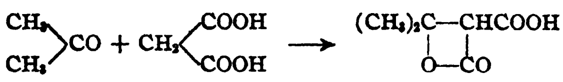
C Meso



$$\begin{array}{l} CH_2\text{——}CH\text{—}COOH \\ |\qquad\quad\ \ | \\ O\text{—}OC\text{—}CH\text{—}CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2\text{——}CH\text{—}COOH \\ |\qquad\quad\ \ | \\ O\text{—}OC\text{—}C{=}CH_2 \end{array}$$

XVI XVII[10]

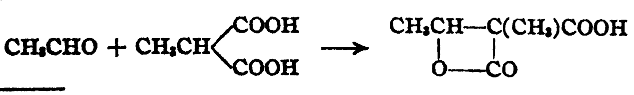
Related to the γ-lactone reaction is the Meldrum[6] synthesis of the β-lactone of β-hydroxyisopropylmalonic acid (XVIII) from a mixture of malonic acid, acetone and acetic anhydride with a small amount of concentrated sulfuric acid



$$\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CO + CH_2<\!\!\begin{array}{l} COOH \\ COOH \end{array} \longrightarrow \begin{array}{l} (CH_3)_2C\text{—}CHCOOH \\ \quad\ \ |\qquad | \\ \quad\ \ O\text{—}CO \end{array}$$

XVIII

Similarly, Ott[7] obtained from methylmalonic acid the α-methylated derivative (XIX) of XVIII. We have found that aldehydes may be used in place of ketones in the Meldrum β-lactonic acid synthesis. Thus, aldehyde reacts with methylmalonic acid to give β-lactonic acid XX



$$CH_3CHO + CH_3CH<\!\!\begin{array}{l} COOH \\ COOH \end{array} \longrightarrow \begin{array}{l} CH_3CH\text{—}C(CH_3)COOH \\ \quad\ \ |\qquad | \\ \quad\ \ O\text{——}CO \end{array}$$

XX

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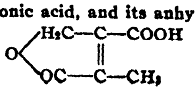
(10) The structure of XVII is uncertain. Itaconic acid, and its anhydride, give citraconic anhydride on distillation, which points to the isomeric  $O<\!\!\begin{array}{l} H_2C\text{—}C\text{—}COOH \\ \qquad\quad \| \\ OC\text{——}C\text{—}CH_3 \end{array}$ as a possible formula.

Until recently, the interpretation of Erlenmeyer[11] has been accepted that alkene formation from salts of β-halogen acids proceeded through a β-lactone. However, Einhorn[12] obtained the β-lactone of the three nitrophenyllactic acids, which decomposed in this manner only at the melting points, and Baeyer and Villiger[13] the β-lactone of β,β-dimethylmalic acid from the corresponding β-halogen acid, which on distillation did not undergo the olefin decomposition. Johansson and Hagman[14] attributed the isolation of these β-lactones that their insolubility in the surrounding media resisted conversion into hydroxy derivatives. By dissolving liberated β-lactones in chloroform as they are formed, they showed that aliphatic β-halogen salts on decomposing in aqueous solution yield mixtures of β-lactones and alkenes. These fatty β-lactones boiled in a vacuum without decomposition and, in some of the reactions, were formed in much larger proportion than the corresponding alkenes. They concluded from these results that such β-bromo salts yield simultaneously a mixture of β-lactone and olefin, but gave no reason for this double mode of decomposition. This is to be sought in the stereostructures of the β-bromo salts. There are good grounds to accept favored, comparatively stable, stereostructures, which represent the maximum degradation of energy, for all saturated aliphatic compounds[15] from the second carbon series on, but, according to the partition principle, the other possible configurations may occur in more or less minor proportions. From this point of view, the β-lactone formation proceeds from the stereostructure in which the halogen and the metallic atom of the salt are in *cis* position to each other. In configurations where these atoms are *trans* to one another, the lactone rings would be formed under such strain that rupture to alkenes and carbon dioxide would occur.

The pyrogenic decomposition of the alkylated β-propiolactonic acids is complicated. Ott[7] showed that β,β-dimethylpropiolactonic acid (XVIII) gave acetone with dimethylketene; its α-methyl derivative (XIX) gave acetone with high boiling products. Although that β-lactonic acid decomposes above its melting point, we found that it can be distilled unchanged in a vacuum. The introduction of an α-methyl into XVIII has increased decidedly the stability of the β-lactone ring toward heat. In striking contrast to the ketonic mode of decomposition, is that of β-lactonic acid XX, whose structure may be derived from that of XVIII by replacing one of the β-methyls by hydrogen. The thermal decomposition of this β-lactonic acid involves merely the elimination of carbon dioxide from the carboxyl, leaving α,β-dimethylpropio-β-lactone (XXI); a fairly stable compound toward heat, since it boils without decomposition

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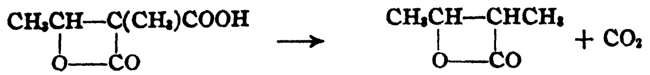
(11) Erlenmeyer, Sr., *Ber.*, **13**, 305 (1880); **14**, 320 (1881).

(12) Einhorn, *ibid.*, **16**, 2208 (1883).

(13) Baeyer and Villiger, *ibid.*, **30**, 1955 (1897).

(14) Johansson and Hagman, *ibid.*, **55**, 647 (1922).

(15) Michael, THIS JOURNAL, **40**, 707 (1918).

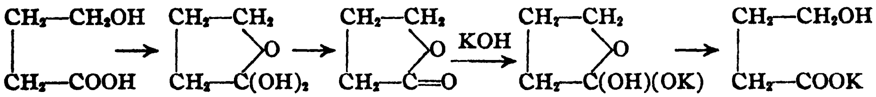


XX XXI

This shows that the unusual fission at the saturated linkages between the α- and β-carbons of XVIII and XIX cannot be ascribed wholly to the lessening of their affinity to each other by the negative influence of the COOH- and COO-groups, since then this influence should be somewhat greater in these lactones than in XX. These reactions further illustrate that if strain in the sense of the Baeyer hypothesis[16] functions it can be only one of the energy factors which enter into the thermal stability of rings.

Upon treatment of β,β-dimethylpropiolactonic acid (XVIII) with cold, aqueous alkali, Meldrum[6] found that it functioned monobasic and when heated with baryta water it decomposed into acetone and malonate. Kandiah[8] stated that β,β-dipropylpropiolactonic acid titrated monobasic with cold alkali and dibasic with the reagent at 100°. We examined the α,β,β-trimethyl derivative XIX toward aqueous caustic soda and observed a still greater stability of the β-lactone ring. With two equivalents at 100° only the mono-sodium salt was produced and from the evaporated dry residue the original monobasic lactonic acid could be recovered. The existing observations on the relative stability of β-lactone rings toward heat and toward alkali with reference to chemical structures show that they run parallel to each other and that they are developed constitutive properties.[16a]

The γ-butyrolactone formation from γ-hydroxybutyric acids,[17] and rupture of the lactone ring by alkali, should be represented as follows



The primary phase of the internal esterification proceeds at the energetic Δ-CO of the acidic group. This carbonyl possesses the chemical potential at the Δ-C and Δ-O atoms for the carbinol O and H atoms to overcome the slight hindrance to the formation of the hydrated pentacyclic lactone ring. The alkali hydrolysis of the lactone ring proceeds through the intermediate addition of alkali at the Δ-CO[18] to pass over into the γ-hydroxy salt. In these reactions the formation of the neutral lactone and hydroxycarboxylate evidently determine the maximum degradation of chemical energy of the systems.

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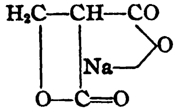
[16] Baeyer, *Ber.*, **18**, 2277 (1885). This chemist [*ibid.*, **23**, 1275 (1890)] made a curious error in endeavoring to interpret the "Strain Theory" in terms of mechanical energy. The tension in a cyclic chain was compared to that in a bent elastic spring, it increasing in each case with the magnitude of the pressure. Baeyer overlooked that the strain in the spring is due to energy exerted externally, while spontaneous ring-formation is caused by internal, intramolecular energy, in a large measure to the free chemical energy and the chemical affinity, *i. e.*, the chemical potential, between the two groups that react directly to form the cyclic system. It can occur only with a decrease of the free chemical energy of the corresponding compound with the open-chain form. The more of the free chemical energy used to complete the closure, the less must be available to hold the terminal groups that unite to form the ring together by bound chemical energy and, therefore, the less will be chemical hindrance to ring-fission. Evidently, this interpretation is the reverse of that implied in the bent spring explanation, where the free energy increases with closure. The magnitude of this chemical hindrance to ring-fission must be one of the major energy factors that determine the stability of rings.—A. M.

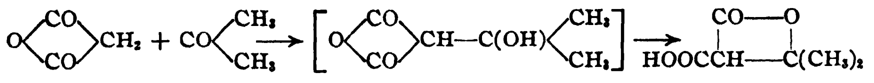
[16a] In opposition to the "Strain Theory" the tetracyclic ring of XIX shows greater stability toward alkaline reagents than the pentacyclic ring of any lactone that has been examined.

[17] Michael, *J. prakt. Chem.*, **60**, 338 (1899); THIS JOURNAL, **40**, 1694 (1918).

These theoretical standpoints permit an insight into several of the above β-lactone reactions. If the primary phase of the action of caustic alkali upon a β-lactone consists in its addition to the ring carbonyl, then the introduction of any chemical influence into the lactone molecule, acting directly or through space, that increases or decreases this additive capacity, must result in a greater lability or stability, respectively, of the lactone ring. The replacement of an α-hydrogen of a lactone by carboxyl should augment the chemical potential of the ring carbonyl for water and alkali, and, accordingly, should lessen the stability of the lactone ring toward aqueous mineral acid and alkali. Toward acid this conclusion holds for β-lactones, but not toward alkali. However, in this case the primary product is the corresponding carboxylate and the not wholly neutralized positive chemical energy of the alkali atom must decrease the facility of addition, depending more or less upon the extent of the free positive energy remaining in the alkali atom. In all cases, the retardation should be noticeable, for the natroxyl group is in the *cis* position to the lactone carbonyl and the metal in the spatially near 5–6 places to the carbon and oxygen of that group. The configuration of the β-propiolactonate may be represented by the formula shown.



According to Ott,[7] malonic acid with acetic anhydride and a little sulfuric acid may give the mixed malonic–monoacetic anhydride. He assumed that malonic anhydride, formed from it by loss of acetic acid, may react with aldolization upon acetone with subsequent rearrangement



It should be stated that the "malonic anhydride" here assumed contained acetyl and that it was also considered a mixed anhydride. Since there is no evidence that sulfuric acid had been entirely removed from the preparation, and the composition of the latter as malonic anhydride is not established, it is evident that the interpretation has no experimental basis. The comparison with the malic β-lactonic acid change is not applicable; if they rearranged similarly the anhydride of isopropylmalonic acid should be formed and not a β-lactone derivative. A simpler and more probable interpretation is that the synthesis of the β-lactone proceeds through a mixed anhydride

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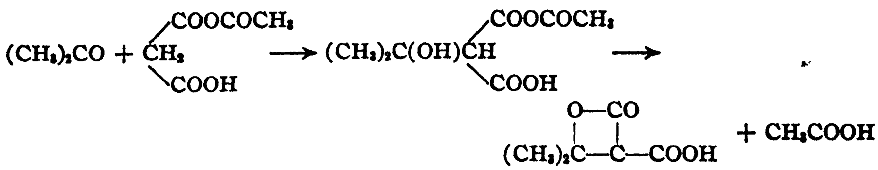
(18) Analogous alkali addition derivatives have been isolated [Michael, *Am. Chem. J.*, 5, 93 (1883); Michael and Lamb, *ibid.*, 31, 552 (1906)].



The probable function of sulfuric acid is to facilitate the formation of the mixed anhydride[19] and to catalyze intramolecular esterification as it does the intermolecular process. In the mixed anhydride the hydrogen attached to the α-carbon becomes more reactive, through replacement of COOH by the more negative radical $COOCOCH_3$, and that replacement of hydroxyl hydrogen by acetyl favors cyclization has been long known.[20]

Experimental

Preparation of Tiglic Acid.—A mixture of 50 g. of methylmalonic acid, 37 g. of paraldehyde, 43 g. of acetic anhydride and 25 g. of acetic acid was heated under a condenser for forty-eight hours, then gently boiled on a sand-bath for four hours. The liquid was distilled with a 15-cm. column until the thermometer read 140°. The residual liquid was then fractionated under reduced pressure, two main fractions being collected; tiglic acid (19 g.), distilling at 90–115° (15 mm.), solidified in the receiver, and a second fraction (13 g.), distilling at 147–150° (10 mm.), which was β-acetoxy-α-methylbutyric acid.

β-Acetoxy-α-methylbutyric acid is a colorless liquid of not unpleasant odor.[21] It readily decomposed into acetic and tiglic acids on distillation at ordinary pressure.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.5; H, 7.5. Found: C, 52.4; H, 7.3.

This method will give a total yield of tiglic acid of approximately 70% of the theoretical. The tiglic acid upon recrystallization melted at 65° and was identical in all other respects with tiglic acid.

Preparation of α-Ethylcrotonic Acid.—A mixture of ethylmalonic acid (38 g.), paraldehyde (22 g.), acetic anhydride (26 g.), and acetic acid (15 g.) was heated as in the preparation of tiglic acid. Upon fractionation there was obtained 20 g. of liquid which distilled at 100–120° (20 mm.), and upon cooling almost completely solidified to large crystals of α-ethylcrotonic acid melting at 42°. There was also obtained a small amount (3.0 g.) of liquid boiling at 156–160° (10 mm.), presumably β-acetoxy-α-ethylbutyric acid.

Action of Aldehydes on Carboxysuccinic Acid. Formaldehyde.—A mixture of 4.0 g. of paraformaldehyde, 8.0 g. of the tricarboxylic acid, 7.0 g. of acetic anhydride and 7.0 g. of acetic acid stood at room temperature for two weeks. The mixture was heated

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(19) Fittig and Stuart [*Ber.*, 16, 1436 (1883); *J. Chem. Soc.*, 48, 403 (1883)] obtained cinnamic and α-methylcinnamic acids from the products of the action of benzaldehyde on sodium malonate, sodium methylmalonate, respectively, and acetic anhydride at room temperature. Under these conditions the aldehyde does not act on the anhydride and sodium acetate mixture and they therefore contended that the syntheses must proceed through the aldehyde and malonate, a view which was practically universally accepted. The writer [*Am. Chem. J.*, 5, 14 (1883)] gave reasons to show that this interpretation was not tenable and that the reaction proceeded through the primarily formed, mixed malonic–acetic anhydride. Later [*J. prakt. Chem.*, 60, 366 (1899); *Ber.*, 34, 918 (1901)], it was proved experimentally that the synthesis with monobasic derivatives takes place through the aldehyde and acid anhydride. The recent preparation and properties of mixed malonic–acetic anhydrides now show unmistakably that the synthesis with malonic derivatives proceeds by action of the aldehyde on mixed anhydrides, not on malonates.—A. M.

(20) Michael, *J. prakt, Chem.*, 44, 113 (1891).

(21) Blaise and Herman, *Compt. rend.*, 146, 1327 (1908); *Ann. chim.*, [8] 20, 189 (1910).

on a water-bath for six hours and boiled under a condenser for an hour. The excess acetic anhydride and acetic acid was removed by distillation under reduced pressure, the flask being placed in a water-bath. There remained a thick sirup containing some unchanged paraformaldehyde, which was removed by warming with excess caustic soda and the acid extracted with ether upon acidifying. On removal of the solvent the sirupy residue deposited crystals (1.0 g.) of an acid (m. p. 161°), which was proved by analysis and a direct comparison to be itaconic acid.

Anal. Calcd. for $C_5H_6O_4$: C, 46.16; H, 4.6. Found: C, 46.26; H, 4.8.

The residual sirup in a desiccator gradually crystallized and was found to be paraconic acid (m. p. 57°); yield 5.0 g.

Anal. Calcd. for $C_5H_6O_4$: C, 46.16; H, 4.6. Found: C, 46.05; H, 4.7.

Acetaldehyde.—A mixture of 3.0 g. of paraldehyde, 5.4 g. of ethinyl tricarboxylic acid, 4.0 g. of acetic anhydride and 5.0 g. of acetic acid stood at room temperature for two weeks. After heating gently on a water-bath for six hours, the excess paraldehyde, acetic anhydride and acetic acid was distilled off under reduced pressure. On cooling, the residue crystallized almost completely and the solid was filtered from the adhering liquid. Recrystallization from a mixture of ether and ligroin gave large prisms of β-carboxy-γ-methylparaconic acid, melting at 165°.

Anal. Calcd. for $C_7H_8O_6$: C, 44.68; H, 4.75. Found: C, 44.52; H, 4.43.

This acid on melting lost carbon dioxide to give γ-methylparaconic acid,[22] melting at 84° after recrystallization from ether–ligroin mixture.

Anal. Calcd. for $C_6H_8O_4$: C, 50.0; H, 5.5. Found: C, 49.81; H, 5.61.

An excellent yield of β-carboxy-γ-methylparaconic acid (approximately 80%) was also obtained from the above mixture by adding a drop of concentrated sulfuric acid and allowing to stand at room temperature for one week. The acid crystallized from the reaction mixture.

Sym-ethane tetracarboxylic acid was prepared by saponifying the ethyl ester with caustic potash and acidifying the dry potassium salt suspended in ether with concentrated hydrochloric acid while cooling well in an ice–salt freezing mixture. The aqueous solution was extracted in the cold with ether in a continuous extractor. The solid acid was obtained from the concentrated ether extract by evaporation in a vacuum desiccator. The crude acid melted at 181° and crystallized from acetone–chloroform solution as fine needles, melting at 183°. By this method a very pure acid can be obtained in excellent yield.

Action of Formaldehyde on Sym-Ethane Tetracarboxylic Acid.—A mixture of 20 g. of the tetracarboxylic acid with 20 g. of acetic anhydride was added to a solution of 7.0 g. of paraformaldehyde in 20 g. of acetic acid and left at room temperature for two weeks. Some evolution of carbon dioxide occurred and after a few days nearly all the solid acid dissolved. The mixture was then warmed on the steam-bath for six hours when evolution of gas almost ceased. The excess acetic acid and acetic anhydride were distilled off under reduced pressure and the residual sirup was taken up in ether and ligroin added. On standing there was deposited 4.5 g. of a mixture of crystalline compounds. Upon fractional crystallization from acetone–ether it gave a compound which melted at 178° with decomposition, to give a second compound melting at 138°. The analysis and properties of the first substance correspond to the dilactone of dimethylol ethinyl tricarboxylic acid (XII).

Anal. Calcd. for $C_7H_6O_6$: C, 45.16; H, 3.28. Found: C, 45.34; H, 3.28.

The compound, melting at 138°, crystallized in large prisms, was soluble in water and analyzed for the γ-dilactone of dimethylol succinic acid (XIII).

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(22) Fittig, *Ann.*, **255**, 1 (1889).

Anal. Calcd. for $C_6H_6O_4$: C, 50.7; H, 4.72. Found: C, 50.72; H, 4.43. *Neutral equivalent.* Calcd. for $C_6H_6O_4$: 142. Found: 140.5.

On treatment with $N/20$ baryta water slow neutralization occurred; 0.06 g. of dilactone was neutralized, added dropwise, in approximately thirty minutes.

After separation of the above acid considerable sirupy material remained. When this was heated under 20 mm. pressure about 5.0 g. distilled over at 210°; the residual resin in the distilling flask decomposed upon further heating. The distillate solidified upon cooling and was separated by fractional crystallization into the dilactone, m. p. 138° (2.5 g.), and an isomeric compound melting at 165°. The latter, an unsaturated acid, crystallized from chloroform in fine needles and gave the following analysis.

Anal. Calcd. for $C_6H_6O_4$; C, 50.7; H, 4.22. Found: C, 50.48; H, 4.34. *Neutral equivalent.* Calcd. for $C_6H_6O_4$: 142. Found: 145.2.

It dissolved immediately in bicarbonate solution with evolution of carbon dioxide and the solution decolorized permanganate solution instantaneously. However, in chloroform solution, it did not readily take up bromine. In analysis and properties it corresponds to the γ-lactone of β-methylol-itaconic (XVII), or -citraconic acid.

Racemization of Dimethylolsuccinic Acid.—The dilactone melting at 138° was dissolved in the calculated amount of 2 N caustic soda and the solution boiled for fifteen minutes. Upon cooling there separated large prisms of an hydrated sodium salt. These crystals were filtered off and, after drying on a porous plate, were analyzed.

Anal. 0.5130 g. of the salt lost 0.2042 g. on drying at 110°, and the dry salt gave 0.1990 g. of anhydrous Na_2SO_4. Calcd. for $C_6H_8O_6Na_2\cdot8H_2O$: H_2O, 39.35; Na, 12.57. Found: H_2O, 39.8; Na, 12.51.

This octahydrate was not formed on standing of the alkaline solution of dilactone for two days in the cold. The mother liquor from the octahydrate was evaporated to dryness and acidified, when the original dilactone (m. p. 138°) was obtained.

γ-Monolactone of Meso Dimethylolsuccinic Acid (XVI).—The disodium salt octahydrate was dried at 110°, the anhydrous salt suspended in ether and acidified with the theoretical amount of hydrogen chloride. Upon evaporation of the ether extract, there was obtained large crystals of the meso hydroxy-lactonic acid, m. p. 122°.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.44; H, 6.17. Found: C, 44.18; H, 5.95. *Neutral equivalent.* Calcd. for $C_6H_{10}O_5$: 160. Found: 159.3.

Upon boiling with acetic anhydride and distilling under reduced pressure this acid gave the unsaturated γ-lactonic acid (XVII) (m. p. 165°).

α-Methyl-α-carboxybutyrolactone.—To a mixture of 20 g. of methylmalonic acid, 20 g. of acetic anhydride, 10 g. of acetic acid and 10 g. of paraldehyde was added one drop of concentrated sulfuric acid. There was an immediate evolution of heat and all the solid acid dissolved. After standing overnight, 0.2 g. of anhydrous sodium acetate was added, in order to convert the sulfuric acid to sodium sulfate, and the excess paraldehyde and acetic acid was removed by heating under reduced pressure, the flask being kept in water at about 80°. The sirupy residue was taken up in ether and ligroin added. Upon standing large crystals of α-methyl-β-hydroxy-α-carboxybutyric acid separated; yield 4 g.

This acid melted at 135° with decomposition. It crystallized in large prisms from chloroform–ligroin.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.44; H, 6.17. Found: C, 44.67; H, 6.44.

When heated at its melting point, under reduced or at atmospheric pressure, it decomposed into acetaldehyde and methylmalonic acid, both of which were identified. There was no identifiable amount of tiglic acid or the β-lactone of β-hydroxy-α-methylbutyric acid obtained in this pyrogenic decomposition.

The β-lactone of α-methyl-α-carboxy-β-hydroxybutyric acid remained as a sirup after removal of crystalline acid.

α-Methylbutyro-β-lactone.—When the sirupy residue was heated above 100° under reduced pressure, decomposition occurred with elimination of carbon dioxide and the above β-lactone distilled over. The original reaction mixture distilled directly gave 70% of this lactone. It is a colorless liquid boiling at 80° (15 mm.)[23] and has a pleasant odor. It is insoluble in cold sodium carbonate but dissolves on warming; it is also soluble in warm caustic soda.

Anal. Calcd. for $C_5H_8O_2$: C, 60.0; H, 8.0. Found: C, 59.84; H, 8.15.

Preparation of Tiglic Acid from α-Methylbutyro-β-lactone.—Seven and one-half grams of the lactone was mixed with 38 cc. of 2 *N* caustic soda and the mixture warmed on a steam-bath. The major part of the lactone rapidly dissolved but there was formed a small amount of deep, yellowish brown resinous material, which had an unpleasant odor, and which was filtered off. The clear, colorless filtrate was evaporated to dryness and the cold sodium salt, suspended in ether, acidified with concentrated hydrochloric acid. The ether extract, which contained β-hydroxy-α-methylbutyric acid, was concentrated and the hydroxy acid distilled under reduced pressures, when it lost water to give almost the theoretical yield of tiglic acid.

Summary

1. The preparation of α-alkyl-α,β-olefinic acids, by the action of aliphatic aldehydes upon mono-alkylmalonic acids, has been described.

2. The method with ethinyl tricarboxylic acid gave γ-lactonic acids; from paraformaldehyde and *sym*-ethane tetracarboxylic acid a γ-dilactonic acid was obtained, which upon heating gave the simplest aliphatic γ-dilactone.

3. The racemic dimethylolsuccinate, obtained from this γ-dilactone upon warming with alkali, reformed the γ-dilactone with mineral acid. On longer heating it racemized partially to the meso salt, which yielded a mono-γ-lactonic acid upon acidifying. These relations offer a rigorous chemical proof that the racemization took place by a rearrangement between a methylol group and a hydrogen atom at one of the asymmetrical carbon centers.

4. It has been shown that aldehyde may replace acetone in the Meldrum malonic synthesis of β-lactonic acids.

5. The thermal and chemical properties of β-lactonic acids in relation to structure have been examined. It has been shown that an intramolecular strain in β-lactone rings can be only one of the energy factors that determine their physical and chemical stability. The relations deduced solely from Baeyer's "Strain Theory" are therefore erroneous.

6. The β-lactone of α-methyl-β-hydroxy-α-carboxybutyric acid has been examined and the preparation of tiglic acid from this acid described.

CAMBRIDGE, MASSACHUSETTS

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[23] Johannson and Hagman, *Ber.*, 55, 647 (1922), gave b. p. 67° (21 mm.).

[CONTRIBUTION FROM UNIVERSAL OIL PRODUCTS CO. RESEARCH LABORATORIES]

Hydrogenation of Aromatic Compounds at Temperatures Close to their Decomposition in the Presence of Catalysts

BY VLADIMIR IPATIEFF

The hydrogenation of aromatic compounds in the presence of mixed catalysts at temperatures close to their decomposition points was first studied by Ipatieff and Klukvin in 1924.[1]

The results of this work led to conclusions which were later confirmed by Ipatieff and Orlow[2] and Kling and Florentin.[3]

However, the work done up to this point did not explain the main problems of destructive hydrogenation in the presence of catalysts. The first question which remained unanswered concerned the hydrogenation of aromatic compounds in the presence of molybdenum oxide catalysts. It is not yet known whether monocyclic aromatic compounds can be hydrogenated under high pressure with other catalysts than nickel or nickel oxide. The first experiments, therefore, concerned the hydrogenation of benzene and xylene under pressure at high temperature (450°F.) in the presence of molybdenum oxide catalysts (MoO_3). It was found that neither benzene nor xylene hydrogenated in the presence of a molybdenum catalyst, while xylene decomposed under these conditions to benzene and toluene.

A second series of experiments dealt with the hydrogenation of naphthalene in the presence of NiO, CuO, Fe_2O_3 and MoO_3 catalysts as well as in their absence, the iron walls of the autoclave acting catalytically.

Since preliminary experiments with fluorene and phenanthrene also resulted in hydrogenation at high temperature in the presence of a molybdenum catalyst, it was concluded that polycyclic aromatic compounds differ from monocyclic compounds under these conditions of hydrogenation.

In the case of naphthalene, it is possible to explain why hydrogenation occurs under the influence of weak catalysts. Naphthalene has two carbon atoms, common to both rings, which differ from the others. One can assume that a molecule of hydrogen is first added to the common carbon atoms (I); the product is immediately isomerized into 1,4-dihydronaphthalene, forming an ordinary double bond in the ring, (II). This compound is easily hydrogenated further to give 1,2,3,4-tetrahydronaphthalene (III).

This assumption is supported by the fact that sodium amalgam causes the hydrogenation of naphthalene to 1,4-dihydronaphthalene (II), which may be transformed into 3,4-dihydronaphthalene with sodium ethoxide.

If the temperature of naphthalene hydrogenation does not exceed 450° tetrahydronaphthalene is obtained almost exclusively. Above 450° the

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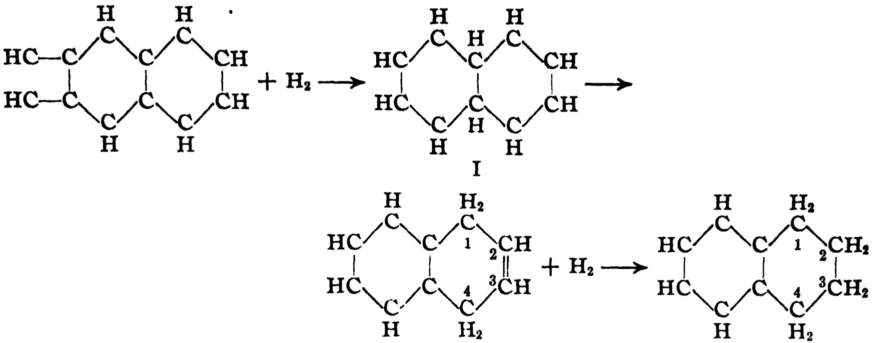
(1) Ipatieff and Klukvin, *Proc. Acad. Sci. Russia*, Leningrad, 1924, **A185**; *Ber.*, **58**, 103 (1925).

(2) Ipatieff and Orlow, *ibid.*, **60**, 1963 (1927); **62**, 719 and 1226 (1929).

(3) Kling and Florentin, *Compt. rend.*, **182**, 526 (1926).



I

II

III

tetrahydronaphthalene formed decomposes into benzene hydrocarbons. It must be noted that decomposition of the tetrahydronaphthalene into benzene hydrocarbons causes the occurrence of naphthenes in all fractions of the product only when using a nickel catalyst. This shows that some molecules of the monocyclic aromatic compounds are hydrogenated during this decomposition.

Another series of experiments was concerned with the hydrogenation of phenol at high temperature in the presence of various catalysts. The investigations of Tropsch,[4] Orlow[2] and Kling and Florentin[3] showed that several hydrocarbons can be obtained under such conditions. Our experiments indicated that at high temperature and pressure (with NiO or MoO_3), hydrogenation of the aromatic ring also occurs, yielding cyclohexane in amounts depending upon the nature of the catalyst used.

The possible hydrogenation of the aromatic ring under such conditions can be explained in the same way as it was in 1905[5] when the hydrogenation of phenol under pressure in the presence of nickel oxide was carried out for the first time. The reaction was explained on the basis of the two *tautomeric forms* of phenol: "true" phenol (enol) and *keto* form. During hydrogenation, "true" phenol is reduced to benzene, with the separation of water. The reaction proceeds at high temperatures without catalysts, under the influence of the iron walls of an autoclave. If a strong hydrogenation catalyst, such as nickel oxide, is present, much cyclohexane is obtained. It should be noted that, at 450–490° under high pressure, cyclohexane is isomerized to methylcyclopentane.[6]

When the hydrogenation of phenol is carried out with MoO_3, Fe_2O_3 or CuO, 10 to 30% cyclohexane is always obtained. Its formation, then, is caused more easily by hydrogenation of the second tautomeric form of phenol—the ketone form—for which a less active catalyst is needed.

My investigations[7] showed that alumina, when not very highly heated

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(4) Tropsch, Third International Conference of Bituminous Coal, Pittsburgh, November, 1931.

(5) V. Ipatieff, *J. Russ. Phys.-Chem. Soc.*, **38**, 89 (1906); *Chem. Abstracts*, **1**, 1538 (1907).

(6) Ipatieff and Dovgelewitch, *Ber.*, **44**, 2987 (1911).

(7) Ipatieff, *ibid.*, **37**, 2986 (1904).

and therefore containing water of hydration, is an active dehydrating catalyst. This fact has been contradicted by the work of Kling and Florentin,[8] who state that alumina prepared at 750° gives high yields of benzene in the hydrogenation of phenol at 490° under high pressure. I can explain this fact that alumina does not act as promoter, but as a porous substance.

Special experiments were made on the hydrogenation of aromatic hydrocarbons in the presence of active catalysts poisoned by thiophene. It was found that although one-ring aromatic hydrocarbons are not hydrogenated at high temperature, naphthalene can be hydrogenated in the presence of thiophene, as well as in its absence. Phenol is hydrogenated in the presence of thiophene, but the action is accompanied by the formation of high-boiling products, presumably esters, etc. Thiophene decomposes completely under these conditions.

Experimental Part

The Hydrogenation of Monocyclic Aromatic Hydrocarbons.—The hydrogenation was carried out in a rotating bomb of the type described by Ipatieff, at 450°, in the presence of catalysts. The data are summarized in Table I.

TABLE I

Expt.	Subs.	Catalyst	Time, hours	Temp., °C.	Pressure, atm. start	Pressure, atm. end	Anal. of gas	Index of ref.	Prod. of reaction
4	Benzene	MoO_3	3	430	100	99	H_2	1.5036/17	Benzene
6	Benzene	MoO_3 50% Al_2O_3 50%	3	400	65	65	H_2	1.5030/18	Benzene
7	Benzene	MoO_3 50% Al_2O_3 50%	3	450	65	64	H_2	1.5029/18	Benzene
9	Xylene	MoO_3	3	450	90	75	H_2 95% Par. 5	....	Benzene Toluene Xylene
19	Xylene	MoO_3 50% Al_2O_3 50%	3	450	100	80	....	....	Benzene Toluene Xylene

As shown in Expts. 4, 6 and 7, benzene cannot be hydrogenated in the presence of molybdenum catalysts. Xylene also fails to hydrogenate under these conditions in the presence of molybdenum catalysts, but decomposes to benzene and toluene (Expts. 9 and 19). The product of reaction dissolves entirely in fuming sulfuric acid and distils at 80–140°. It was separated into: (1) fraction boiling at 80–81° which solidified at 0°, and (2) fraction boiling at 108–112° (with nitric acid forms dinitrotoluene).

The Hydrogenation of Naphthalene.—The experiments on the hydrogenation of naphthalene in the presence of different catalysts were carried out in the rotating autoclave at 450–475°. The data obtained are shown in Table II.

Catalyst MoO_3 was precipitated from solution of ammonium molybdate by addition of nitric acid, and dried for thirty-six hours at 210°. $MoO_3Al_2O_3$ consists of a mechanical mixture of the precipitated MoO_3 and Al_2O_3.

$Fe_2O_3Al_2O_3$ and $CuOAl_2O_3$ were precipitated from a solution of mixed nitrate salts of these metals by addition of ammonium hydroxide and dried at 250°.

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[8] Kling and Florentin, International Congress on Bituminous Coal, Pittsburg, November, 1931.

TABLE II

Expt.	Catalyst	Time, hrs.	Temp., °C.	Press., atm. init.	Press., atm. end	% of HC	Analysis of hydrocarbon fractions: Distillation I	Distillation II	Index of refraction 26° I	Index of refraction 26° II	Specific gravity 26° I	Specific gravity 26° II
7	NiO, 50% Al_2O_3, 50%	25	400	80	20	95	77–83	...	1.4441	....	....	....
8		2	450	64	20	93	75–78	78–81	....	....	....	....
12	MoO_3, 50% Al_2O_3, 50%	2	425	65	35	88	70–77	77–82	1.4642	1.4789	0.8125	0.8291
13		2	450	65	35	92	70–78	78–82	1.4671	1.4679	.8155	....
10		3	475	65	35	95	70–78	78–82	1.4679	1.4840	....	....
16	MoO_3	2	450	65	31	83	69–81	81–88	....	1.4650	....	....
17	MoO_3	2	450	65	35	..	70–79	79–83	....	....	....	....
22	Fe_2O_3, 50% Al_2O_3, 50%	2	450	65	55	22	75–82	82–84	1.4815	1.4362	....	....
23		2	450	65	57	..	70–72	72–81	1.4430	1.4750	.8337	....
20	Without catalyst	2	450	65	52	25	75–81	81–84	1.4730	1.4935	.8454	....
21		2	450	65	53	..	...	...	....	....	....	....
25	Al_2O_3	2	450	65	57	10	70–84	...	1.4755	....	....	....
27	Al_2O_3	2	450	65	58	8	...	...	....	....	....	....

Expt.	Phenol (100 g.) Analysis of hydrocarbon fractions after treatment I and II fractions with fuming H_2SO_4 (20%): Distillation 1	Distillation 2	Index of refraction 26° 1	Index of refraction 26° 2	Specific gravity 26° 1	Specific gravity 26° 2	Product of destr. hydrogenation contained, %: Benz. HC	Cyclohexane	Analysis of gas, %: H_2	C_nH_{2n+2}
7	75–84	...	1.4248	....	....	....	10	90	96	1.6
8	75–84	...	1.4246	....	....	....	12	88	96	1.8
12	75–77	...	1.4163	....	....	....	88	12	...	...
13	74–77	81–83	1.4140	1.4244	0.7583	....	84	16	94.6	1.2
10	74–77	81–83	1.4230	....	....	....	85	15	..	...
16	75–76	79–80	1.4189	1.4240	.7504	0.7620	70	30	..	...
17	...	79–80	....	1.4215	.7326	....	80	20	93.8	1.8
22	75–82	...	1.4230	....	....	....	84	16	94.3	4.0
23	75–82	...	1.4283	....	....	....	84	16	...	...
20	77–79	79–81	1.4249	1.4270	.7634	....	80	20	94.4	3.9
21	...	...	....	....	....	....	..	..	..	...
25	75–82	...	1.4186	....	....	....	88	12	..	...
27	...	...	....	....	....	....	..	..	..	...

$NiOAl_2O_3$.—The precipitation (nitrate salts) was made by addition of ammonium carbonate, the product dried for seventeen hours at 210° and in a stream of air for five hours at 400°. All catalysts were used in amount of 10% of the substance.

From Table II one can see that $NiOAl_2O_3$ catalyst (Expt. 21) gave 38% of the fraction boiling at 196–208°. The analysis and properties prove the presence of *tetralin*. Found: C, 90.76; H, 8.78. Other products were identical with those obtained by Klukvin and myself, *i. e.*, consist of aromatic hydrocarbons—benzene, toluene, etc. In order to ascertain whether other hydrocarbons are present in the aromatic fractions they were treated with 15% fuming sulfuric acid. The hydrocarbons insoluble in sulfuric acid are ***naphthenes;*** they did not react with the nitrating mixture and analysis gave: boiling point 76–104°, d_4^0 0.7630; n_D^{26} 1.4215; C, 85.82; H, 14.78.

Contacting with MoO_3 as catalyst for a short time, the yield of tetralin increased to 76% (Expt. 24). In this case benzene hydrocarbons are obtained in small amount. When hydrogenation is carried out for a long time the first fraction (80–120°) contains about 10% of naphthenes (after treatment with fuming sulfuric acid), confirmed by analysis: boiling point 72–78°, d_4^0 0.7547, n_D^{26} 1.4070; C, 85.25; H, 14.78.

Analysis showed that methylcyclopentane had been formed by isomerization of cyclohexane.

Experiments 17, 25, 8, 9 and 23 showed that the same results were reached when catalysts MoO_3 or $MoO_3Al_2O_3$ were used and when the time of hydrogenation was extended. At 475° very little tetralin remained; the aromatic hydrocarbon fractions do not contain other hydrocarbons.

Experiments 12 and 13 (catalyst $CuOAl_2O_3$) and Experiments 9, 10 and 11 (catalyst $Fe_2O_3Al_2O_3$) showed that the formation of tetralin also takes place and aromatic hydrocarbons are obtained. Analysis of different fractions (catalyst $Fe_2O_3Al_2O_3$) gave: Fraction 80–110°, C, 91.03; H, 8.76; corresponding to C_7H_8. Fraction 125–150°, C, 90.61; H, 8.83; corresponding to C_8H_{10}. Fraction 175–190°, C, 89.63; H, 8.63; corresponding to C_9H_{12}.

Experiment 26 shows that at 475° in the absence of a catalyst we have the same picture of hydrogenation.

The Influence of Thiophene upon the Hydrogenation of Naphthalene.—It was found that, at high temperatures of hydrogenation, the thiophene does not affect the reaction appreciably. Thus in the hydrogenation of naphthalene ($NiOAl_2O_3$) 38% of tetralin was obtained whereas in the presence of thiophene 33% was obtained.

The Hydrogenation of Phenol.—The hydrogenation of phenol proceeded under the conditions as described in the case of naphthalene. The data are summarized in Table II. Experiment 8 showed the reaction with $NiOAl_2O_3$ proceeded within two hours only when the temperature was 400°. After-treatment of hydrocarbons (95%) with 15% fuming sulfuric acid yielded 90% cycloparaffins—cyclohexane and methylcyclopentane.

Experiments 12, 13, 16 and 17 showed the hydrogenation of phenol in the presence of catalysts $MoO_3Al_2O_3$ and MoO_3; MoO_3 is a more active catalyst and the amount of naphthenes obtained increased slightly.

Analysis of fractions (Experiment 13) after treatment with sulfuric acid proves that we have naphthenes: Fraction 74–77°, C, 85.37; H, 14.30. Fraction 81–83°, C, 84.94; H, 14.60. Calcd. for C_nH_{2n}: C, 85.62; H, 14.38.

Analysis of fractions (Experiment 16) after treatment with sulfuric acid gave: Fraction 73–76°, C, 85.05; H, 14.70. Fraction 79–80°, C, 84.87; H, 14.56.

Experiments 22 and 23 (catalyst $Fe_2O_3Al_2O_3$) showed that the amount of phenol decomposed is considerably smaller (about 25%).

If phenol is hydrogenated *without a catalyst*, almost the same result is obtained as when iron oxide was used. After treatment of the fractions (Expt. 20) boiling 75–81° and 81–84° with 15% sulfuric acid, a hydrocarbon was obtained which did not react with the nitrating mixture. Its analysis showed that it was cyclohexane: C, 84.92; H, 14.61.

Experiments 25 and 27 Catalyst Al_2O_3.—The formation of an unsaturated hydrocarbon becomes noticeable, since the hydrocarbons obtained decolorize permanganate solution. After treatment with fuming sulfuric acid (15%) a hydrocarbon is obtained which does not react with the nitrating mixture and is a mixture of cyclohexane and methylcyclopentane.

The Hydrogenation of Phenol in the Presence of Thiophene.—If the hydrogenation of phenol is carried out in the presence of MoO_3 and 1% thiophene, the same results are obtained. From 200 g. of phenol at 450° for two hours, 160 g. of a product was obtained which contained only 12 g. of unchanged phenol, and hydrocarbons distilled at 69–84°; 26% hydrocarbons remained. They distil at 77–81°, n_D^{26} 1.4215. The hydrocarbons do not react with the nitrating mixture and must be cyclohexane with a small amount of methylcyclopentane. With catalyst $NiOAl_2O_3$ and addition of 1% thiophene the hydrogenation of phenol also takes place but the yield of hydrocarbons decreases to 50%. The rest consisted of unchanged phenol and a small amount of high boiling products. It may be supposed that they consist of phenyl ether and cyclohexylcyclohexanol.

Summary

1. The hydrogenation of monocyclic benzene hydrocarbons cannot take place in the presence of molybdenum catalysts prepared by precipitation in the usual way.

2. During destructive hydrogenation with catalysts, the combination of hydrogen with aromatic compounds occurs first, followed by the decomposition of the hydrogenated product.
3. Active catalysts may hydrogenate the benzylene ring, at the time of its formation, and during the decomposition of a hydrogenated product.
4. The destructive hydrogenation of phenol is due to its tautomeric form.
5. The presence of thiophene does not change the rate of destructive hydrogenation of naphthalene.
6. Thiophene decreases the yield of hydrocarbons during the hydrogenation of phenol.

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The Oxidation of Sym-Triiodophenol[1]

BY W. H. HUNTER AND MARY L. MORSE

The present research upon the oxidation of *sym*-triiodophenol was undertaken for the purpose of ascertaining further facts concerning the nature and relative stability of triiodo Type A and diiodo Type B radicals.

A preliminary qualitative survey was made of the oxidation of *sym*-triiodophenol in non-aqueous or in aqueous media by several oxidizing agents.

The oxidation of *sym*-triiodophenol in alkaline solution by potassium ferricyanide was then chosen for further study. The products of this reaction were a large quantity of Lautemann's Red, a small quantity of the dinuclear quinone, 2,6,2′,6′-tetraiododiphenoquinone,[2] and an unstable compound which was not isolated. No phenoxyquinones were found.

Experiments were also carried out for the purpose of showing the relative oxidizing power of the crude oxidation products obtained from the respective oxidations of *sym*-trichloro-, tribromo-, and triiodophenols in glacial acetic acid by a large excess of chromium trioxide. The crude oxidation from the trichlorophenol showed the presence of about 97% of the mononuclear dichloroquinone, which has long been known to be the chief oxidation product formed under these conditions, whereas the crude

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(1) The work described in this paper formed a part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Mary L. Morse in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1929. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. SMITH.

(2) Kammerer and Benzinger [*Ber.*, **11**, 557 (1878)] assigned this formula to a substance which they obtained by the action of potassium tri-iodide solution on a boiling solution of phenol in sodium carbonate. However, the work of Hunter and Woollett indicated that the material obtained by Kammerer and Benzinger was Lautemann's Red. In this case, 2,6,2′,6′-tetraiododiphenoquinone is a new compound.

oxidation product of triiodophenol showed the presence of only 86% of mononuclear diiodoquinone. The crude oxidation product of tribromophenol, with 74% of mononuclear dibromoquinone, proved to be more similar to the oxidation product of triiodophenol than to that of the trichlorophenol.

The results of this research upon the oxidation of *sym*-triiodophenol indicate a pronounced tendency toward the rapid formation of Type B radicals, when this compound is treated with reagents capable of disengaging the hydrogen of the phenolic hydroxyl group. Since no phenoxyquinones were isolated, it is assumed that an iodinated Type A radical is very much less stable than its trichloro and tribromodimethoxy analogs. On the other hand, a comparison of the relative oxidizing power of the crude oxidation products of *sym*-trichloro, tribromo and triiodophenols indicates that polymerization of Type B radicals, proceeding concurrently with oxidation, is a more pronounced property of diiodo Type B radicals than of dichloro Type B radicals.

Another characteristic of the diiodo Type B radical is brought out by a comparison of certain of the products isolated in this study, with the oxidation products of pyrogallol dimethyl ether, as reported by Graebe and Hess,[3] and of tribromoresorcinol studied by Davis and Hill.[4] All of these products may be considered to be derivable from the polymerization of Type B radicals, although it is noteworthy that the mode of polymerization is apparently capable of variation, for from the diiodo Type B radicals there result both carbon to carbon and carbon to oxygen ties, the latter type predominating, whereas the dimethoxy Type B radical and the dibromoreso Type B radical exhibit a carbon to carbon type of polymerization.

No compounds ascribable to a carbon to carbon polymerization of Type B radicals were isolated in the work of Hunter and Levine[5] on the oxidation of tribromopyrogallol dimethyl ether, or in that of Hunter and Minerva Morse[6] on the oxidation of *sym*-trichlorophenol. All of the compounds isolated in these investigations must be looked upon as resulting from the carbon to oxygen type of polymerization.

The variation in the mode of polymerization evidenced by the types of polymers described above may be considered as due in part at least to the character of the Type B radicals involved. Thus, if a Type B radical of a given kind were more stable in a benzenoid than in a quinoid form, the corresponding polymer would be of the carbon-oxygen type, whereas if a Type B radical existed predominantly in the quinoid form, the carbon-carbon type of polymerization would occur.

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(3) Graebe and Hess, *Ann.*, **340**, 232 (1905).

(4) Davis and Hill, This Journal, **51**, 500 (1929).

(5) Hunter and Levine, *ibid.*, **48**, 1608 (1926).

(6) Hunter and Morse, *ibid.*, **48**, 1615 (1926).

The results of this investigation indicate that: (1) if the triiodo Type A radical is capable of existence, it is less stable than the Type A radicals previously studied in this Laboratory; (2) the diiodo Type B radical, on the other hand, is more stable and exhibits a greater tendency toward polymerization than its dichloro analog; (3) diiodo Type B radicals are capable of polymerizing both carbon-carbon and carbon-oxygen, the latter representing the predominating tendency.

Experimental Part

The Effect of Various Oxidizing Agents on Sym-Triiodophenol.—The attempted oxidation of triiodophenol in glacial acetic acid by sodium nitrite resulted in the replacement of one of the iodine atoms by a nitro group. Nitro compounds of this type also resulted from the reaction between triiodophenol in carbon tetrachloride and nitrogen trioxide. No oxidation products were isolated in either case. The results of this investigation were in agreement with those reported earlier by Raiford and Heyl.[7]

In the oxidation of triiodophenol in benzene by lead dioxide a buff colored amorphous material, presumably polydihalogenophenylene oxide resulting from the catalytic decomposition of the salts of *sym*-triiodophenol, was the only product formed in appreciable amount. About 50% of the triiodophenol was recovered unchanged after a twenty-four hour reaction period. This reaction was not studied further.

The oxidation of triiodophenol in glacial acetic acid by chromium trioxide resulted in the formation of a large quantity of *m*-diiodo-*p*-quinone, some amorphous material and a small quantity of tetraiododiphenoquinone.

Triiodophenol was oxidized in neutral solution by potassium permanganate. The chief product of this reaction was a reddish amorphous mixture. This was reduced by treatment with sulfur dioxide, and extracted with acetone. The insoluble amorphous material amounted to about 75% of the theoretical yield calculated on the basis of the exclusive formation of the Type B radical. This material was probably the amorphous oxide. It was not investigated further. The acetone extract was evaporated to a small volume. A gum-like material was left which was purified by repeated crystallizations from ethyl acetate. The crystalline product melted at 260–263°, although some decomposition and evolution of iodine were noticeable at around 245°. This compound was found to be identical with the 2,6,2′,6′-tetraiododiphenol to be described below.

Anal. Calcd. for $C_{12}H_6O_2I_4$: I, 73.62. Found: (Carius) I, 73.56, 73.52.

Oxidation of Sym-Triiodophenol in Alkaline Solution by Potassium Ferricyanide

Preparation of the Oxidation Product or "Red Mixture."—A solution of 70 g. (10 equivalents) of potassium ferricyanide in 300 cc. of water was added in one lot with stirring to a solution of 10.00 g. (1 equivalent) of *sym*-triiodophenol dissolved in 15 cc. of 2 *N* potassium hydroxide (1.5 equivalents) and 200 cc. of water. A heavy reddish brown precipitate appeared immediately. The mixture was filtered, and the residue washed thoroughly with water. The filtrate contained some iodine but no organic material.

The precipitate, which will be called the "red mixture," was dried to constant weight at 60°. The average weight of the product at this point (for several runs) was 7.56 g. The theoretical weight calculated on the basis of the exclusive formation of Type B radicals, and the compounds which might result from subsequent polymerization of these, was 7.29 g.

Reduction of the "Red Mixture" and Isolation of 2,6,2′,6′-Tetraiododiphenol.—Ten lots of "red mixture" prepared as described above were combined while still moist and suspended in a liter of water. A solution of 14.4 g. of hydrazine sulfate in 400 cc. of 2 *N* potassium hydroxide was added to this suspension and the mixture was placed on a steam-bath. After thirty to forty minutes the solution was decanted from the residue and the latter was thoroughly extracted with warm 1 *N* potassium hydroxide. The filtrate and washings were combined and acidified with acetic acid. A white precipitate was formed, which amounted to 4.3 g. or 5.6% yield of alkali soluble product.

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[7] Raiford and Heyl, *Am. Chem. J.*, **43**, 393 (1910); **44**, 209 (1910).

This material was difficultly soluble in most organic solvents, but was purified by several crystallizations from ethyl acetate. It melted at 260–265° with noticeable decomposition at 245°. A molecular weight determination was impossible due to insolubility of the substance.

Anal. Calcd. for $C_{12}H_6O_2I_4$: I, 73.62. Found: (Carius) I, 73.64, 73.50.

2,6,2′,6′-Tetraiododiphenoquinone.—Two hundred cc. of a saturated solution of 2,6,2′,6′-tetraiododiphenol in glacial acetic acid was treated with 0.5 g. (50 equivalents) of chromium trioxide in 1 cc. of water and 25 cc. of glacial acetic acid. A drop of concentrated sulfuric acid was added to the mixture which was stirred for five minutes and filtered; 0.12 g. of a dark green crystalline product was obtained. The mother liquor was diluted with water but no further precipitation occurred. The crystalline product could not be purified further, due to its insolubility. It did not melt.

Anal. Calcd. for $C_{12}H_4O_2I_4$: I, 73.82. Found: (Carius) I, 73.09, 73.13.

Anal. (Hydrazine method for quinoid oxygen). Calcd. for $C_{12}H_4O_2I_4$: O, 4.65. Found: O, 4.66, 4.58.

Evidence for the Presence of an Unstable Compound in "Red Mixture."—A sample of freshly prepared "red mixture" was extracted with dry ether and filtered rapidly. The residue, a clean, red powder, was extracted with dry benzene, yielding a deep red solution. Gradual evaporation of the solvent at room temperature and atmospheric pressure gave deep red crystals, with a gold sheen. This substance decomposed without melting, and all attempts to purify it by recrystallization failed as the dry material changed rapidly to a reddish brown amorphous powder. A solution of the red crystals left a varnish-like deposit upon evaporation of the solvent, and no crystalline material could be obtained after this change had occurred. Several attempts were made to determine the quinoid oxygen content of this substance. The results were variable, but the highest value obtained was roughly 5.4%. The calculated quinoid oxygen content of tetraiododiphenoquinone is 4.65%, of *m*-diiodo-*p*-quinone, 8.88%, and of the as yet unknown triiodophenol iodide, 5.38%.

Comparison of the Quinoid Oxygen Content of the Crude Oxidation Products of Sym-Trichloro, Tribromo and Triiodophenols

Preparation of the Oxidation Product of the Sym-Trihalogenated Phenol.—1.00 gram of the *sym*-trihalogenated phenol was dissolved in a small quantity of glacial acetic acid at 50°. A solution of 19 equivalents of chromium trioxide in an equal weight of water was added to this solution all at once. After a few seconds (5–10 in the case of the trichlorophenol, 20 in the other two cases) the mixture was poured with

TABLE I

CRUDE OXIDATION PRODUCTS

Halogenated phenol, *sym*-tri-	Chloro	Bromo	Iodo
Crude oxidation product, g.	0.40	0.35	0.66
Yield, %	45.2	44.2	85.2
Quinoid oxygen in ox. prod.,[a] %	17.53	8.94	7.61
m-Dihalogeno-*p*-quinone in ox. prod., %	97.1–97.4	70.5–79.6	84.6–86.9

[a] Average of four or five determinations.

stirring into 200 cc. of water. The crude oxidation product which separated was filtered by suction within one half hour, and dried in a desiccator over concentrated sulfuric acid for about eighteen hours. The experimental data are given in Table I.

Summary

1. The oxidation of *sym*-triiodophenol results in the formation of mononuclear quinone, dinuclear quinone of the cedriret type, chromopolydihalogenophenylene oxide (Lautemann's Red) and an unstable compound which has not been isolated.

2. 2,6,2′,6′-Tetraiododiphenol and 2,6,2′,6′-tetraiododiphenoquinone have been isolated for the first time.

3. The crude oxidation product formed in the oxidation of *sym*-triiodophenol in glacial acetic acid by an excess of chromium trioxide is poorer in mononuclear quinone than that obtained under the same conditions by the oxidation of *sym*-trichlorophenol.

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Some Tolyl Derivatives of Germanium[1]

BY J. K. SIMONS, E. C. WAGNER AND J. H. MÜLLER

Numerous phenyl but relatively few tolyl derivatives of germanium are known.[2]

No ortho or meta tolyl germanium compounds have been reported. A number of para tolyl compounds, mostly of mixed types, have been described by Tabern, Orndorff and Dennis,[3] Schwarz and Lewinsohn,[2] Bauer and Burschkies,[2] and Shelton.[4] Most tetraarylgermanes have been prepared from germanium tetrahalide by arylation either with Grignard compounds or with aryl halides and sodium,[2] both methods giving low yields.[5]

In the present study the interaction of germanium tetrachloride and arylmagnesium bromide led to incomplete arylation, with formation of triarylgermanium halide; a similar result was reported by Morgan and Drew[5] in the preparation of tetraphenylgermane. This procedure was tried unsuccessfully also for the preparation of triphenyl-*m*-tolylgermanium

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(1) From the thesis presented by J. K. Simons in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Pennsylvania, June, 1933.

(2) "Gmelins Handbuch der anorganischen Chemie," System-Number 45, "Germanium," 8th ed., Verlag Chemie, Berlin, 1931, pp. 53–57; R. Schwarz and Lewinsohn, *Ber.*, **64**, 2352 (1931); Kraus and Nutting, THIS JOURNAL, **54**, 1622 (1932); Flood, *ibid.*, **54**, 1663 (1932); Bauer and Burschkies, *Ber.*, **65**, 956 (1932).

(3) Tabern, Orndorff and Dennis, THIS JOURNAL, **47**, 2039 (1925); **49**, 2512 (1927).

(4) Shelton, paper presented at the Washington meeting of the American Chemical Society.

(5) Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925). No other investigators report yields on tetraaryl compounds.

from triphenylgermanium bromide and *m*-tolylmagnesium bromide. The interaction of germanium tetrachloride and *p*-tolylmagnesium bromide further afforded an interesting example of exchange of halogen, the major product being tri-*p*-tolylgermanium bromide. An analogous result was obtained by Bauer and Burschkies[2] for the reaction between cyclohexylmagnesium bromide and germanium tetrachloride.

A much more satisfactory procedure is that first used for tetraphenyltin by Chambers and Scherer[6] and extended by Kraus and Foster[7] to the preparation of tetraphenylgermanium, the first-formed Grignard compound being treated with zinc chloride, and the resulting zinc aryl (without isolation) treated with germanium tetrahalide. By this method there were obtained tetra-*p*-tolyl-, tetra-*m*-tolyl-, and tetra-*o*-tolylgermane in yields of 65, 75 and 30%, respectively. In each case some of the corresponding di-tolyl was isolated. No tri-*p*-tolylgermanium chloride was found, but both tri-*m*-tolyl- and tri-*o*-tolylgermanium chlorides were isolated as by-products due to incomplete arylation. The zinc aryl procedure was used also for the preparation of triphenyl-*m*-tolylgermanium.

The dearylation of tetraarylgermanes by bromine was effected for tetra-*p*-tolylgermanium by Schwarz and Lewinsohn[8] and for the tetra-*o*- and tetra-*m*-tolyl compounds in the present study. In each case the main product was triarylgermanium bromide, some nuclear bromination occurring with the *o*-tolyl compound. Hydrolysis of tri-*m*-tolyl- and tri-*p*-tolylgermanium bromide by aqueous alkali or by alcoholic silver nitrate yielded the corresponding tritolylgermanium oxide, $(Ar_3Ge)_2O$. Similar treatment of the *o*-tolyl chloride gave the hydroxide, Ar_3GeOH.

Controlled dearylation by the action of gaseous hydrogen bromide upon tetraaryl compounds, in preliminary experiments with tetraphenyl- and tetra-*p*-tolylgermanium, effected replacement of one aryl group by bromine, yielding triarylgermanium bromide and aromatic hydrocarbon, both of which can be isolated. It is the purpose of work now in progress to attempt the use of this reaction in a study of the relative reactivities of various aryl groups when attached to germanium, analogous to the work of Kharasch, Bullard, Gilman and others,[9] on organic compounds of other elements.

Experimental

General

Germanium Tetrachloride.—Winkler[10] found that dry distillation of a mixture of mercuric chloride and germanium sulfide yields germanic chloride. Trials showed that recovery of germanium is high but the product somewhat impure. The results of dis-

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(6) Chambers and Scherer, This Journal, **48**, 1054 (1926).

(7) Kraus and Foster, *ibid.*, **49**, 459 (1927).

(8) Schwarz and Lewinsohn, *Ber.*, **64**, 2354, 2358 (1931).

(9) See, *e. g.*, Kharasch and Flenner, This Journal, **54**, 674 (1932); Bullard and Holden, *ibid.*, **53**, 3150 (1931); Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932).

(10) Winkler, *J. prakt. Chem.*, [2], **36**, 188 (1887).

tillations of mixtures of germanite and mercuric chloride showed that ordinary distillation from a flask transposed as high as 73% of the germanium to chloride; heating the mixture in a sealed tube at 260–290° transposed 97% of the germanium to chloride. This reaction might be used to prepare large quantities of the chloride and for analytical purposes is even more promising.

The germanium tetrachloride needed for the work described was prepared from 4.2 kg. of 100-mesh germanite (6.45% GeO_2) by decomposition with concentrated nitric acid, digestion of the dried insoluble residue with concentrated hydrochloric acid and distillation. The distillate of crude chloride was washed with concd. hydrochloric acid to remove arsenious chloride[11] and distilled through an all glass eight-ball Snyder column. The product (490 g., 87.5% recovery) boiled 83.0–83.8° corr. and gave no test for arsenic in the last fraction.

Bromotoluenes were obtained from Eastman Kodak Co. Anhydrous zinc chloride (Baker U. S. P.) was fused and then crushed and kept in a desiccator over phosphorus pentoxide. Eastman anhydrous ether was kept over sodium just before use. Tetraphenylgermane and triphenylgermanium bromide were prepared according to Kraus and Foster.[12] Grignard reagents were prepared in the usual way and in an atmosphere of nitrogen.

Analysis.—After a consideration of the available methods for the determination of germanium in organic compounds,[13] it seemed preferable to estimate carbon and hydrogen rather than germanium. Trials of a modification of the usual wet oxidation methods, using concd. and fuming sulfuric acid with solid ammonium persulfate followed by evaporation to GeO_2 in a silica beaker heated laterally by a ring-burner, gave results in three to five hours which were reproducible but low by about 0.6% due to mechanical loss during expulsion of fumes. Accordingly carbon and hydrogen were determined by the micro-method of Pregl.[14] Both a porcelain and a platinum boat were used, combustion occurring more readily in the latter. It was found advisable to cover the sample with a layer of previously ignited finely ground copper oxide. The compounds were with one or two exceptions difficult to burn, the last traces of carbon being extremely resistant to combustion, so that it was necessary to heat the tube until it just began to soften. Some of the substances with lower melting points ignited with a flash when too rapidly heated, but even with these all of the carbon could be burned only on strong ignition. The analyses reported below are in each case the average of three acceptable determinations.

Preparation of Tolyl Compounds of Germanium

Tetratolylgermanes—General Procedure.—Interaction of germanium tetrachloride, aryl bromide (*o*-bromotoluene), and sodium yielded unsatisfactory results. Interaction of the Grignard reagent and germanium tetrachloride yielded triarylgermanium bromide as the main product. The modified zinc aryl procedure described below, essentially that of Kraus and Foster,[15] was found satisfactory. The Grignard reagent dissolved in ether in a three-necked one liter flask equipped with a stirrer, reflux condenser and dropping funnel, reacted in an atmosphere of nitrogen with an ether suspension of zinc chloride. After refluxing for one-half to one hour the ether was replaced by toluene (or xylene). To the cooled mixture was added a solution of germanium tetrachloride in the same solvent. After standing overnight the mixture was heated on the water-bath for three hours and then stirred and refluxed for fifteen to twenty hours. Mechanical stirring was used throughout and was found to be noticeably more efficient than agitation by a stream of nitrogen. Ammonium chloride and dilute hydrochloric acid were used for the hydrolysis and yielded cleaner products than did 2 *N* sulfuric acid. The upper layer was dried by calcium chloride and distilled to a residue under reduced pressure. Further details are recorded in the descriptions of the individual compounds.

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[11] Allison and Müller, THIS JOURNAL, 54, 2833 (1932).

[12] Kraus and Foster, *ibid.*, 49, 459, 460 (1927).

[13] Morgan and Drew, *J. Chem. Soc.*, 127, 1767 (1925); Dennis and Hance, THIS JOURNAL, 47, 374 (1925); Kraus and Brown, *ibid.*, 52, 3693 (1930); Bauer and Burschkies, *Ber.*, 65, 960 (1932); Tabern and Shelberg, *Ind. Eng. Chem.*, *Anal. Ed.*, 4, 402–403 (1932).

[14] Pregl, "Quantitative Organic Micro-analysis," tr. by Fyleman, P. Blakiston's Co. and Son, Philadelphia, 1924, pp. 15–72.

[15] Kraus and Foster, THIS JOURNAL, 49, 459 (1927).

p-Tolyl Derivatives

Tetra-*p*-tolylgermanium.—*p*-Bromotoluene (100 g.), zinc chloride (33 g.) and germanium tetrachloride (13 g.) were treated as outlined above. The residue was dissolved in 50–60 cc. of benzene. To the warm solution was added an equal volume of 58–70° ligroin, the whole chilled strongly, and the separated solid washed with cold ligroin. The mother liquors yielded more crystals by the same procedure. The yield of pure product was 65%. It melted at 229° on the Dennis "melting point bar" and at 227° corr. in the usual apparatus.

Anal. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46. Found: C, 76.5; H, 6.47.

Tri-*p*-tolylgermanium Bromide.—Germanium tetrachloride (10.8 g.) was treated in ether solution with the Grignard reagent from 50 g. of *p*-bromotoluene. The mixture, after standing for two days, was refluxed for four hours. The ether was then distilled off and the residue heated at 110° for three hours.[16] The mass was taken up in benzene, decomposed with 2 *N* sulfuric acid, and the benzene layer dried with calcium chloride. The oily residue after distilling off the benzene was diluted with 20 cc. of 58–70° ligroin and the tetra-*p*-tolylgermanium filtered off; yield, 3.2 g.; 14.6%.

The mother liquors on vacuum distillation yielded (a) a small amount of *p*-bromotoluene, b. p. (760 mm.) 160–190°, (b) di-*p*-tolyl, b. p. (1–2 mm.) 100–125°, m. p. 117–121° from ligroin, and (c) a viscous oil of b. p. (1 mm.) 229–234° which after five recrystallizations from 90–120° ligroin was obtained as a crystalline solid of m. p. 130° corr. Mixed with a specimen of tri-*p*-tolylgermanium bromide (m. p. 127–128°) made according to Schwarz and Lewinsohn,[17] the melting point was 128–129°. This with the analytical and molecular weight values reported below identified the product as tri-*p*-tolylgermanium bromide. The yield after the first crystallization was 10.3 g. or 48%.

Anal. Calcd. for $C_{21}H_{21}GeBr$: C, 59.20; H, 4.97; mol. wt., 426. Found: C, 59.5; H, 5.24; mol. wt. (cryoscopic in benzene), 403, 404.

Tri-*p*-tolylgermanium Oxide.—Slightly impure tri-*p*-tolylgermanium bromide (1.9 g. from the Grignard reaction) was refluxed for ten hours with 40 cc. of 0.5 *N* aqueous sodium hydroxide. The resulting solid was filtered off and the filtrate titrated with 0.5 *N* hydrochloric acid. (Bromine found by titration, 18.3; calcd., 18.8.)

The white solid after drying and several crystallizations from 90–120° ligroin, and from a mixture of ligroin and methyl alcohol, melted at 147–148° corr.

Anal. Calcd. for $C_{42}H_{42}Ge_2O$: C, 71.23; H, 5.98; mol. wt., 708. Found: C, 70.6; H, 6.09; mol. wt. (Rast), 753; (cryoscopic in benzene), 714.

Tri-*p*-tolylgermanium oxide is a white densely crystalline solid, crystallizing in well-developed very small anisotropic prisms. It is insoluble in water; very slightly soluble in methyl and ethyl alcohol; and soluble in hot ligroin and cold benzene.

This compound was also made by the action of alcoholic silver nitrate on the bromide. The crystals obtained melted at 148–150° corr.

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(16) Kraus and Flood showed this procedure to be advantageous in the preparation of tetraethylgermanium [THIS JOURNAL, 54, 1636 (1932)].

(17) R. Schwarz and Lewinsohn, Ref. 2, p. 2354.

m-Tolyl Derivatives

Tetra-*m*-tolylgermanium.—The Grignard reagent from *m*-bromotoluene (75 g.), zinc chloride (30–33 g.), and germanium tetrachloride (10–11 g.) reacted as described above. The ether was removed by gentle heating (below 80°). After the usual further procedure there was obtained a final residue which was purified by crystallization from 58–70° ligroin; yield, 75%. Repeated crystallizations from 58–70° ligroin or a mixture of 90–120° ligroin and alcohol yielded the pure compound of melting point 146° corr.

Anal. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46; mol. wt., 437. Found: C, 76.5; H, 6.61; mol. wt. (cryoscopic in benzene), 405.

Tetra-*m*-tolylgermanium is a white solid crystallizing from ligroin in long thin needles, which exhibit parallel extinction. It reacts with bromine to form tri-*m*-tolylgermanium bromide. It is insoluble in water; very slightly soluble in hot or cold methyl alcohol; soluble in ligroin or carbon tetrachloride, and very soluble in benzene or toluene.

Tri-*m*-tolylgermanium Chloride.—The mother liquors from crystallization of several preparations of tetra-*m*-tolylgermanium were vacuum distilled. Di-*m*-tolyl was isolated boiling at 120–125° at 1–2 mm. and at 280–290° at atm. pressure. The only other isolable product was a viscous oil boiling at 221–224° (1–2 mm.). Crystallization from dry methyl alcohol gave fine silky needles melting at 79° to a cloudy liquid which cleared at 90°. Analysis identified this as tri-*m*-tolylgermanium chloride with a trace of a bromine-containing impurity.

Anal. Calcd. for $C_{21}H_{21}GeCl$: C, 66.10; H, 5.55; mol. wt., 381. Found: C, 66.4; H, 5.51; mol. wt. (Rast), 445.

This compound was made also by warming tri-*m*-tolylgermanium oxide (see below) with concd. hydrochloric acid and alcohol on the water-bath. Evaporation of the alcohol and crystallization from methyl alcohol gave a product of m. p. 84–85° corr. A mixed melting point with the chloride obtained as by-product was 81.5–82.5° corr.

Tri-*m*-tolylgermanium chloride is a white solid crystallizing in fine optically active needles exhibiting parallel extinction. It is soluble in ligroin or benzene, and nearly insoluble in cold methyl alcohol.

Tri-*m*-tolylgermanium Bromide.—Tetra-*m*-tolylgermanium (25 g.) dissolved in 400 cc. of carbon tetrachloride was treated with 9.2 g. of bromine in 50 cc. of carbon tetrachloride added over a period of two hours. On refluxing the color gradually disappeared. After filtering with charcoal, the straw-yellow solution was distilled under slightly reduced pressure. *m*-Bromotoluene distilled at 128–129° at 135 mm.; b. p. 181–184° at 763 mm.; yield, 4.5 g. (46%).

The oily residue (25.0 g.) was crystallized from 400 cc. of hot methyl alcohol; yield, 15.8 g.; 65%. Two more crystallizations raised the melting point to 78.0–78.9° corr. The boiling point was 222–223° at 1 mm.

Anal. Calcd. for $C_{21}H_{21}GeBr$: C, 59.20; H, 4.97. Found: C, 59.1; H, 4.90.

Tri-*m*-tolylgermanium bromide is finely crystalline and white, but acquires a slight brown tinge on standing. It crystallizes in small, imperfectly formed, anisotropic needles. It is soluble in carbon tetrachloride, benzene and ether.

Tri-*m*-tolylgermanium Oxide.—The impure bromide (3.4 g.) from the mother liquors of the above preparation was shaken and then warmed with 150 cc. of a 1% alcoholic silver nitrate solution. The filtered solution was evaporated, the residue washed with water, taken up in benzene, dried with calcium chloride, and the solvent evaporated (yield, the theoretical). The product, crystallized three times from ligroin, melted at 125.0–125.2° corr.

Anal. Calcd. for $C_{42}H_{42}Ge_2O$: C, 71.23; H, 5.98; mol. wt., 708. Found: C, 71.0; H, 5.93; mol. wt. (cryoscopic in benzene), 686.

Tri-*m*-tolylgermanium oxide crystallizes in thick ill-formed crystals. It reacts with concd. hydrochloric acid in alcoholic solution to form tri-*m*-tolylgermanium chloride as described above. It is soluble in alcohol and benzene, and is insoluble in water.

Triphenyl-*m*-tolylgermanium.—Triphenylgermanium bromide (5 g.) and *m*-tolylmagnesium bromide reacted in the usual manner[18] and gave a product melting at 132–133° corr. Its analysis is reported below. A further crystallization from methyl alcohol raised its melting point to 136–138° corr. Attempts to repeat this experiment using twice the quantity of bromide were unsuccessful due to the large amount of triphenylgermanium oxide which was formed from unreacted bromide. The following procedure was better.

The zinc aryl compound from 20 g. of *m*-bromotoluene reacted in benzene solution with 6.0 g. of triphenylgermanium bromide. The mixture was refluxed for fourteen hours and then decomposed with ammonium chloride. The residue from distillation of the benzene layer deposited crystals which were washed with alcohol and dried; yield, 5.3 g.; 86%; m. p. 144–147° corr. After two crystallizations from alcohol and ligroin the substance was extracted eleven times with small quantities of methyl alcohol. This served to separate a high melting insoluble impurity and yielded a specimen of triphenyl *m*-tolylgermanium, resembling the above product under the microscope, and melting at 136.5–138.5° corr. A mixed melting point test gave the value 136–138° corr.

Anal. Calcd. for $C_{25}H_{22}Ge$: C, 75.99; H, 5.62; mol. wt., 395. Found: C, 75.9; H, 5.97; mol wt. (cryoscopic in benzene), 379.

Triphenyl *m*-tolylgermanium crystallizes from hot methyl alcohol in small strongly anisotropic needles which exhibit parallel extinction. It is soluble in benzene and hot ligroin; insoluble in cold ligroin, methyl and ethyl alcohols. Small amounts are best crystallized from methyl alcohol; larger amounts from a mixture of alcohol and ligroin.

o-Tolyl Derivatives

Tetra-*o*-tolylgermanium.—This compound was prepared according to the general procedure. The quantities were the same as for the *m*-tolyl compound; xylene was used as solvent in place of toluene. The oily residue was diluted with 20 cc. of 58–70° ligroin, and on standing yielded a solid product which was filtered off and washed with 58–70° ligroin. The melting point was 162–165° corr.; yield, 7.8 g.; 30%. The product was crystallized by boiling with 150 cc. of alcohol and enough benzene to clear the solution, which was filtered hot and chilled, yielding 4.9 g. of white, dense crystals of m. p. 173–174.5° corr. A specimen purified by repeated crystallization from 90–120° ligroin and then from a mixture of alcohol and benzene had a sharp melting point of 175–176° corr.

Anal. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46; mol. wt., 437. Found: C, 76.9; H, 6.48; mol. wt. (cryoscopic in benzene), 392.

When crystallized from alcohol and benzene, crystals of the tetra-*o*-tolyl compound appear slowly and are usually badly developed, although their hexagonal character is easily observed under the microscope. The compound is insoluble in water, cold alcohol and light ligroin; slightly soluble in hot alcohol; and soluble in carbon tetrachloride, benzene, xylene or hot ligroin.

Tri-*o*-tolylgermanium Bromide.—A solution of tetra-*o*-tolylgermanium (4.0 g.) when refluxed with an equivalent quantity of bromine in 50 cc. of pure carbon tetrachloride was rapidly decolorized with the evolution of hydrogen bromide. Distillation

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(18) Orndorff, Tabern and Dennis, THIS JOURNAL, 49, 2513 (1927).

of the solution yielded at 205–210° (1 mm.) a colorless oil with a bluish fluorescence. The product contained bromine. The molecular weight in benzene was 409; calcd. for $C_{21}H_{21}GeBr$, 426.

Tri-*o*-tolylgermanium Chloride.—The ligroin extract from the preparation of tetra-*o*-tolylgermanium was distilled *in vacuo*. After removal of some di-*o*-tolyl (b. p. (760 mm.) 272–282°), three fractionations at 1–2 mm. yielded finally a yellowish resinous oil with a bluish fluorescence which boiled at 229–235° at less than 1 mm. Its analysis indicated it to be probably a mixture of tri-*o*-tolylgermanium chloride and tetra-*o*-tolylgermanium.

Anal. Calcd. for $C_{21}H_{21}GeCl$: C, 66.10; H, 5.55; for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46. Found: C, 74.0; H, 6.19.

Slow evaporation of an alcohol solution of this product deposited a solid which after crystallization from alcohol melted at 157–161°; it had the characteristic crystal form of tetra-*o*-tolylgermane under the microscope. The mother liquor from the first separation of the product was freed from alcohol and the residue distilled. It boiled at 216–222° at 1 mm. and treated with alcoholic silver nitrate yielded tri-*o*-tolylgermanium hydroxide, indicating it to be probably tri-*o*-tolylgermanium chloride.

Tri-*o*-tolylgermanium Hydroxide.—Tri-*o*-tolylgermanium chloride (4.0 g.) obtained as just described (b. p. (1 mm.) 215–219°) was treated with an excess of alcoholic silver nitrate. The filtrate, worked up as outlined under tri-*m*-tolylgermanium oxide, yielded an oily residue which would not crystallize but which distilled at 212–214° (1 mm.) as a resinous oil. On standing it became crystalline. From hot methyl alcohol it deposited as an amorphous powder. Qualitative tests showed the absence of halogen.

Anal. Calcd. for $C_{21}H_{22}GeO$: C, 69.46; H, 6.11; mol. wt., 363. Found: C, 69.6; H, 6.12; mol. wt. (cryoscopic in benzene), 344.

The Controlled Action of Hydrogen Bromide on Tetraarylgermanium Compounds

Tetraphenylgermanium.—An excess of hydrogen bromide was passed at room temperature through a solution of tetraphenylgermane (3.0 g.) in 100 cc. of chloroform. The solution was distilled to a residue which was crystallized twice from 90–120° ligroin. The crystals of triphenylgermanium bromide melted at 138.2° corr.

Tetra-*p*-tolylgermanium.—A 30% excess of hydrogen bromide reacted at room temperature with the germane (3.0 g.) in 100 cc. of chloroform. The solution was fractionally distilled and 3.2 cc. collected between 66 and 110°. Refractionation of this product yielded toluene, identified as 2,4-dinitrotoluene, m. p. 70–71° corr.[19]

The residue of 3.1 g. (2.9 g. calcd.) was crystallized from 58–70° ligroin. It melted at 124–128.5° obs.; mixed with tri-*p*-tolylgermanium bromide (m. p. 128–129.5° obs.) the melting point was 127–129.5° obs.

Summary

1. The following new tolyl compounds of germanium have been prepared and characterized: tetra-*o*-tolylgermanium, tetra-*m*-tolylgermanium, tri-*o*-tolylgermanium bromide, tri-*m*-tolylgermanium bromide and chloride, tri *o*-tolylgermanium hydroxide, tri-*m*-tolylgermanium oxide, tri-*p*-tolylgermanium oxide, triphenyl-*m*-tolylgermanium.

2. The zinc aryl procedure of Kraus and Foster has been used successfully in the preparation of tetratolylgermanes, including tetra-*p*-tolylgermanium, and the mixed compound triphenyl-*m*-tolylgermanium.

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[19] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. I, 1904, p. 202.

3. Interaction of germanium tetrachloride and *p*-tolylmagnesium bromide yielded principally tri-*p*-tolylgermanium bromide, indicating the probable cause of low yields of tetraarylgermanes hitherto obtained by this method.

4. Controlled action of hydrogen bromide on tetraphenyl- and tetra-*p*-tolylgermanium yielded the corresponding triarvlgermanium bromide and aromatic hydrocarbon.

PHILADELPHIA, PENNSYLVANIA

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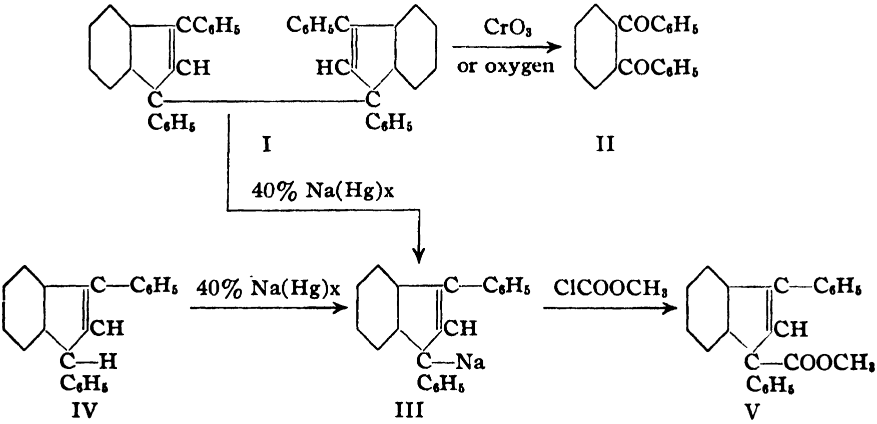
Rearrangements of the Polyines. V. Reactions of Bis-1,1'-(1,3-diphenylindenyl)

BY M. T. GOEBEL AND C. S. MARVEL

Bis-1,1'-(1,3-diphenylindenyl) (I) has recently been prepared[1] for the purpose of comparing it with the isomeric hydrocarbon $C_{42}H_{30}$, which is formed by the rearrangement of tetraphenyldiphenylethinylethane.[2] A comparison of the physical properties of these two hydrocarbons showed that they were not identical. The present study of the chemical reactions of bis-1,1'-(1,3-diphenylindenyl) has shown that it resembles the hexaarylethanes rather than the hydrocarbons produced when tetraaryldiethinylethanes undergo rearrangement.



Bis-1,1'-(1,3-diphenylindenyl) (I) was oxidized readily by chromic acid to give almost quantitative yields of *o*-dibenzoylbenzene (II) and no *o*-benzoylbenzoic acid was obtained. Under the same conditions Moureu's hydrocarbon[2] yielded no *o*-dibenzoylbenzene but did give *o*-benzoylbenzoic

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(1) Halley and Marvel, THIS JOURNAL, **54**, 4450 (1932).

(2) Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927); Wieland and Kloss, *Ann.*, **470**, 217 (1929); Munro and Marvel, THIS JOURNAL, **54**, 4445 (1932).

acid. The bisindenyl was rapidly oxidized to *o*-dibenzoylbenzene by oxygen at the temperature of boiling xylene. Some oxygen was absorbed by a cold solution of the bisindenyl but no definite oxidation products were isolated.

The bisindenyl gave a faintly yellow colored solution in xylene at room temperature. Heating this solution out of contact with air caused the color to deepen and subsequent cooling caused this color to fade. However, the color change was not strictly reversible and continued heating and cooling changed the bisindenyl into a gummy solid.

The bisindenyl was slowly cleaved by 1% sodium amalgam but readily by 40% amalgam or sodium–potassium alloy to give a metal derivative (III) which was identical with the one prepared from 1,3-diphenylindene (IV). The identity of the two metal derivatives was shown by converting them to the same methyl ester of 1,3-diphenylindene-1-carboxylic acid (V).

These reactions of bis-1,1'-(1,3-diphenylindenyl) show that it contains a weak central carbon–carbon linkage and apparently dissociates to an unstable free radical at elevated temperatures. It is related in structure to the diarylvinyldiarylmethyl radicals of Ziegler[3] and to the triphenylindenyl of Kohler.[4]

Experimental

Bis-1,1'-(1,3-diphenylindenyl).—The procedure of Halley and Marvel[2] was followed but somewhat larger runs were made. The product was obtained in yields of 65% of the theoretical amount, m. p. 195–196°. It was also readily prepared by treating 1,3-diphenylindene with 40% sodium amalgam and treating the resulting metal alkyl with tetramethylethylene bromide.

Oxidation. 1. With Potassium Dichromate.—A solution of 1 g. of the hydrocarbon and 5 g. of potassium dichromate in 50 cc. of glacial acetic acid was boiled under a reflux condenser for about ten hours. The solution was poured into water, the precipitate was collected on a suction filter and then recrystallized from alcohol. The yield was 0.8 g. of *o*-dibenzoylbenzene, m. p. 145–146°. The identification was made by taking a mixed melting point of this material with *o*-dibenzoylbenzene prepared according to the method of Guyot and Catel.[5]

2. With Oxygen.—A solution of the bisindenyl in xylene did not absorb a measurable amount of oxygen at 30°. However, at the temperature of boiling xylene, the solution did absorb oxygen and the bisindenyl was oxidized to *o*-dibenzoylbenzene.

A solution of 0.5 g. of the bisindenyl in 30 cc. of xylene was placed in a flask attached to a gas buret filled with oxygen. The solution was heated to boiling and shaken vigorously for about thirty minutes. The solution was maintained at the boiling point of xylene by heating the flask occasionally with a small flame. The mixture was cooled, and the oxygen absorption (92 cc., 0°, 760 mm.) measured. The treatment was repeated but no further oxygen was absorbed. During the first treatment with oxygen there was a series of color changes which seemed of interest since they occurred in every trial. The solution was pale yellow at the beginning. During the first three minutes of the reaction, this color faded until the solution was entirely colorless. Then during the next five minutes a deep red color developed. At the end of thirty minutes this color had faded and the solution was again yellow in color. From the reaction mixture 0.3 g. of *o*-dibenzoylbenzene was obtained.

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[3] Ziegler, *Ann.*, **434**, 34 (1923).

[4] Kohler, *Am. Chem. J.*, **40**, 217 (1908).

[5] Guyot and Catel, *Bull. soc. chim.*, [3] **35**, 1135 (1906).

A solution of 1 g. of the bisindenyl in 200 cc. of chloroform was shaken in an atmosphere of dry oxygen for three days. A deep red color developed in the solution and about 20 cc. of oxygen (0°, 760 mm.) was absorbed. Evaporation of the solution gave a red gum from which no crystalline material could be separated.

Effect of Heat.—A solution of the bisindenyl in xylene became deeper yellow in color on heating and the color faded on cooling. After two or three times the deeper color no longer faded. Evaporation of the solution gave a very impure sample of the bisindenyl. Prolonged heating in xylene changed the bisindenyl to gummy products which could not be identified.

Reduction.—Reduction of the bisindenyl by boiling 1 g. with 1.5 g. of phosphorus in 5 cc. of constant boiling hydriodic acid and 50 cc. of glacial acetic acid gave 0.8 g. of 1,3-diphenylhydrindene (m. p. 156–157°) which was identical with a sample of this material which was prepared by the method of Ziegler, Grabbe and Ulrich.[6]

Cleavage with Alkali Metals. With 1% Sodium Amalgam.—A solution of 1 g. of the bisindenyl in 250 cc. of dry ether gave a distinctly yellow colored solution when shaken with 10 cc. of 1% sodium amalgam for thirty minutes.

With 40% Sodium Amalgam.—A solution of 1.5 g. of the bisindenyl in 250 cc. of dry ether was shaken with 10 cc. of 40% sodium amalgam. The characteristic yellow color developed in ten minutes. The mixture was shaken overnight, the sodium derivative was treated with methyl chloroformate and a 20% yield of 1-carbomethoxy-1,3-diphenylindene was obtained. The ester was characterized by comparing it with the material described below.

With Liquid Sodium–Potassium Alloy.—A solution of 1 g. of the bisindenyl in 250 cc. of ether was shaken with 5 g. of liquid sodium–potassium alloy. A yellow color developed at once. After about thirty minutes the metal derivative was converted to the carbomethoxy derivative. The yield was 0.6 g. If the alloy was allowed to react for a longer period a secondary reaction occurred and no ester could be obtained.

1-Carbomethoxyl-1,3-diphenylindene.—A solution of 2 g. of 1,3-diphenylindene in 250 cc. of dry ether was shaken with 10 cc. of 40% sodium amalgam. The reaction seemed to be complete in about an hour, as little hydrogen was evolved after that time. At the end of about twenty-four hours, the excess amalgam was frozen and the yellow solution of the sodium derivative was decanted. An atmosphere of dry nitrogen was maintained over the solution during these operations. A slight excess of methyl chloroformate was added to the solution and then the solution was washed with water, dried over magnesium sulfate and the solvent evaporated. The residue was recrystallized from a mixture of ethyl acetate and methanol. The yield was 1.5 g. of a product melting at 99–100°.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.62; H, 5.56; mol. wt., 326. Found: C, 84.66, 84.58; H, 5.62, 5.51; mol. wt. (Rast), 334, 317.

The corresponding acid could not be obtained by treating the metallic derivative with dry carbon dioxide. When these experiments were performed the carbon dioxide discharged the color of the metal alkyl solution but on working up the reaction mixture only the original 1,3-diphenylindene was recovered. Attempts to hydrolyze the methyl ester with alcoholic potassium hydroxide and subsequent liberation of the acid by addition of mineral acid gave a gum which could not be purified.

Summary

Bis-1,1′-(1,3-diphenylindenyl) has been found to have many properties

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(6) Ziegler, Grabbe and Ulrich, *Ber.*, **57**, 1983 (1924).

which are characteristic of hexaarylethanes and must therefore be classed as a new type of hydrocarbon which contains an active carbon–carbon single bond.

URBANA, ILLINOIS
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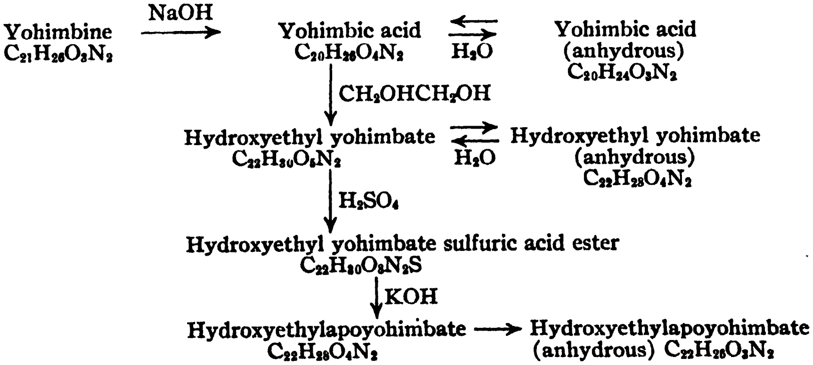
[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Some Hydroxy and Amino Esters of Yohimbic Acid

BY DAVID E. WORRALL

Yohimbine is an optically active alkaloid occurring in the bark of the African yohimbus tree. The present investigation is concerned with an attempt to increase the anesthetic action by the introduction of certain groups. Yohimbic acid exists in two forms differing one from the other by a molecule of water. Yohimbine is the methyl ester of anhydrous yohimbic acid and results whether one starts with hydrated or anhydrous yohimbic acid. Similarly ethyl alcohol forms an ester with yohimbic acid corresponding to the anhydrous form. On the contrary, propyl and butyl alcohols form esters that retain the additional molecule of water.[1]

It has been found in the present investigation that yohimbic acid forms esters with the polyhydric alcohols, ethylene glycol, trimethyleneglycol and glycerol, as well as with ethylene chlorohydrin, reacting with one equivalent of each. The resulting esters are derivatives of the hydrated form of yohimbic acid. The additional molecule of water is easily eliminated by drying in a vacuum over phosphorus pentoxide, a process that is reversed by exposing the product to air. The new esters turn yellow on exposure to light, form water-soluble salts with acids, etc. Esters are formed with sulfuric acid that on hydrolysis with alkali regenerate sulfuric acid, thereby producing an unsaturated group in the alkaloid. This reaction results in a base containing one molecule less of water than the



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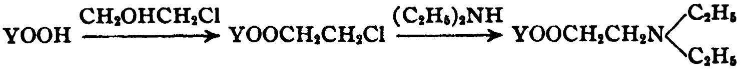
(1) Barger and Field, *J. Chem. Soc.*, **123**, 3003 (1923).

original substance. The new substance is still capable of losing a molecule of water, changing from the hydrated to anhydrous form. Therefore, the term *apo* introduced by Barger and Field,[2] who discovered this reaction with sulfuric acid, has been used to designate the unsaturated base. The scheme shown, using ethylene glycol with yohimbic acid, illustrates the changes and relationships involved.

The ester obtained from ethylene chlorohydrin is capable of condensing with secondary amines, thereby producing groups found in local anesthetics of the novacaine type.



$$\mathrm{YOOH} \xrightarrow{\mathrm{CH_2OHCH_2Cl}} \mathrm{YOOCH_2CH_2Cl} \xrightarrow{\mathrm{(C_2H_5)_2NH}} \mathrm{YOOCH_2CH_2N}\begin{matrix}\diagup \mathrm{C_2H_5} \\ \diagdown \mathrm{C_2H_5}\end{matrix}$$

Experimental

Yohimbic acid was prepared by the alkaline hydrolysis of yohimbine hydrochloride:[3] 5-g. samples were weighed out, mixed with 20–25 cc. of the appropriate alcohol and saturated with hydrogen chloride gas. The crude ester solutions after a week's standing were added slowly to a moderately large volume of water containing an excess of ammonia and recrystallized from dilute alcohol; yield of purified material 3–3.5 g.

TABLE I

ESTERS OF YOHIMBIC ACID

Substance	Formula	M. p., °C.	Cryst. form	Analyses, % Calcd. C	H	Found C	H
α-Chloroethyl	$C_{22}H_{29}O_4N_2Cl$	119–120	Stout flat needles	Cl,	8.4	Cl,	8.4
α-Hydroxyethyl	$C_{22}H_{30}O_5N_2$	132–135	Prismatic needles	65.7	7.5	65.2	7.6
α-Hydroxypropyl	$C_{23}H_{32}O_5N_2$	135–138	Flat needles	66.4	7.7	66.0	7.8
α,β-Dihydroxypropyl	$C_{23}H_{32}O_6N_2$	111–112	Microscopic	63.9	7.4	63.5	7.5

The new esters, if dried in a vacuum over sulfuric acid, gain weight on exposure to the atmosphere until one molar equivalent of water has been absorbed.

α-Hydroxyethyl Yohimbate Sulfuric Acid Ester.—One gram of hydroxyethyl yohimbate was dissolved in 10 cc. of cold concd. sulfuric acid, warmed to room temperature and poured on cracked ice. The product was recrystallized from water, separating in the form of microscopic crystals melting at 288–289°.

Anal. Calcd. for $C_{22}H_{30}O_8N_2S$: S, 6.6. Found: S, 6.7.

α-Hydroxyethyl Apoyohimbate.—The sulfuric acid ester was heated for a few minutes with dilute alkali. Extraction with ether removed the apo compound, which was recrystallized from alcohol, separating in glistening irregular plates melting at 117–118°, and darkening rapidly on exposure to light or heat.

Anal. Calcd. for $C_{22}H_{28}O_4N_2$: C, 68.7, H, 7.3. Found: C, 68.2, H, 7.4.

The hydrochloric acid salt, prepared by adding a few drops of the acid to a hot alcoholic solution of the ester, separates from solution in clusters of flat needles melting with decomposition at 292–294°.

Anal. Calcd. for $C_{22}H_{28}O_4N_2\cdot HCl$: Cl, 8.4. Found: Cl, 8.2.

The amine derivatives were prepared by dissolving chloroethyl yohimbate in an excess of the appropriate amine and heating the mixture in a sealed tube. The contents were then dissolved in acid and precipitated in the customary manner with ammonia. The anhydrous form in each case was used for analysis.

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(2) Barger and Field, *J. Chem. Soc.*, **123**, 1040 (1923).

(3) Spiegel, *Ber.*, **36**, 169 (1903); Field, *J. Chem. Soc.*, **123**, 3004 (1923)

TABLE II

AMINO ESTERS OF YOHIMBIC ACID

Substance	Formula	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H	Time required for formation
α-Diethylaminoethyl	$C_{26}H_{37}O_3N_3$	76– 78	71.1	8.4	70.8	8.9	3 hours
α-Allylaminoethyl	$C_{25}H_{33}O_3N_3$	124–126	70.9	7.8	70.4	7.9	8 hours
α-Piperidinoethyl	$C_{27}H_{39}O_4N_3$	129–131	69.1	8.3	69.4	8.6	10 minutes

α-Diethylaminoethyl Apoyohimbate.—The diethylamino compound (5 g.) was dissolved in 50 cc. of cold concd. sulfuric acid. After standing for ten minutes the mixture was added to cracked ice, thereby producing a sticky gelatinous precipitate. This product was converted into the apo compound by heating with 2% alcoholic potash; yield approximately 1 g. The analytical sample was dried over sulfuric acid immediately before use. It separates from alcohol in lustrous microscopic crystals melting at 80–82°.

Anal. Calcd. for $C_{26}H_{35}O_2N_3$: C, 74.1; H, 8.3. Found: C, 73.6; H, 8.5.

These yohimbine compounds react smoothly with methyl iodide, forming addition products which were obtained as follows. To approximately 0.5 g. of the yohimbine derivative dissolved in 5 cc. of acetone was added an excess of methyl iodide. The resulting oil was separated, washed with acetone and dried at 105–110°.

TABLE III

METHYL IODIDES OF YOHIMBATES

Substance, yohimbate	Formula	Iodine, % Calcd.	Found	M. p., °C.
α-Hydroxypropyl	$C_{23}H_{32}O_5N_2 \cdot CH_3I$	22.6	22.7	Indefinite
α,β-Dihydroxypropyl	$C_{23}H_{32}O_6N_2 \cdot CH_3I$	22.1	22.2	Indefinite
α-Allylaminoethyl	$C_{25}H_{35}O_4N_3 \cdot CH_3I$	21.8	21.6	Indefinite
α-Piperidinoethyl	$C_{27}H_{39}O_4N_3 \cdot 2CH_3I$	33.1	32.9	218–219
α-Diethylaminoethyl	$C_{26}H_{39}O_4N_3 \cdot 2CH_3I$	34.3	34.6	217–218
α-Diethylaminoethyl apo-	$C_{26}H_{37}O_3N_3 \cdot 2CH_3I$	35.1	35.3	179–180

The hydrochloric acid salts were prepared by bubbling hydrogen chloride gas through an acetone solution of the yohimbate and drying in the oven at 105°.

TABLE IV

HYDROCHLORIDES OF YOHIMBATES

Substance, yohimbate	Formula	Chlorine, % Calcd.	Found	M. p., °C.
α-Allylaminoethyl	$C_{25}H_{35}O_4N_5 \cdot 2HCl$	13.8	14.0	263–264° + foaming
α-Piperidinoethyl	$C_{27}H_{39}O_4N_3 \cdot 2HCl$	13.1	13.0	212–214° + dec.
α-Diethylaminoethyl	$C_{26}H_{39}O_4N_3 \cdot 2HCl$	13.4	13.2	198–200° + foaming

Anal. Calcd. for $C_{26}H_{39}O_4N_3 \cdot 2HCl$: C, 58.9; H, 7.7. Found: C, 58.6; H, 7.8.

Several of these substances have been sent for physiological investigation to Dr. Albert G. Young of Boston for whose assistance in securing the gift of a generous quantity of this alkaloid from Hoffmann-Laroche of Nutley, New Jersey, I am very grateful.

Summary

Esters of yohimbic acid with ethylene glycol, trimethylene glycol, glycerol and ethylene chlorohydrin have been synthesized.

The ester with ethylene chlorohydrin has been found to react with allylamine, piperidine and diethylamine.

Certain salts and derivatives of the resulting hydroxy and amino esters were prepared.

MEDFORD, MASSACHUSETTS
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Studies in the Rearrangements of Phenyl Ethers. The Action of Aluminum Chloride on Butyl Phenyl Ethers

BY RICHARD A. SMITH

The action of aluminum chloride on phenyl ethers has been studied extensively; this reaction is now reasonably clear and is known as the Fries migration.[1]

The isomerization of phenyl ethers to substituted phenols has received but little study; the two rearrangements appear, at the present time, to have many characteristics in common. There are undoubtedly many recorded instances of reactions in which phenyl ether isomerization took place due to the presence of an aluminum chloride catalyst. The transitory nature of the ether in most cases prevented the observation of the rearrangement as such. In 1892 Hartmann and Gattermann[2] in utilizing the action of aluminum chloride at elevated temperatures to hydrolyze phenyl ethers to phenols and alkyl halides noticed, in one case, the formation of a small quantity of a substituted phenol. This will be referred to in greater detail later. Ether rearrangements with the aid of aluminum chloride have been reported by Huston.[3] The author has reported the synthesis of thymol and an isomer by the catalytic isomerization of isopropyl *m*-cresyl ether with aluminum chloride.[4]

In this communication it is desired to show extensions of the method to rearrangements of different types of alkyl phenyl ethers. Ethers in which the carbon atom of the alkyl group attached to the ether oxygen was, respectively, primary, secondary and tertiary were studied. The three butyl ethers, iso, secondary and tertiary, were selected. A second purpose is to attempt to clarify contradictory evidence in the literature pertaining to para iso and tertiary butyl phenols.

The first purpose of the report was fulfilled by synthesizing the three designated butyl phenyl ethers in a conventional manner. The isobutyl phenyl ether has been prepared previously.[2,5]

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(1) Kraenzlein, "Aluminiumchlorid in der organischen Chemie," Verlag Chemie, G. m. b. H. Berlin, 1932.

(2) Hartmann and Gattermann, *Ber.*, **25**, 3531 (1892).

(3) R. C. Huston, Indianapolis Meeting of the American Chemical Society, 1931.

(4) Smith, THIS JOURNAL, **55**, 849 (1933).

(5) Riess, *Ber.*, **3**, 780 (1870); Bamberger, *ibid.*, **19**, 1820 (1885); Perkin, *J. Chem. Soc.*, **69**, 1250 (1896); Senkowski, *Ber.*, **24**, 2974 (1891).

The three ethers were treated in the cold with anhydrous aluminum chloride and the reaction products isolated and identified as substituted phenols.

Hartmann and Gattermann in reporting the small quantity of substituted phenol they obtained from isobutyl phenyl ether state it to be *p*-isobutylphenol. The melting point they cite is in agreement with that in the literature for *p*-isobutylphenol. Kraenzlein[1] in commenting on their work states that the action is a splitting off of isobutylene and readdition of this compound and phenol to yield *p*-tertiary-butylphenol. The compound prepared by Hartmann and Gattermann is reported as the tertiary product in Beilstein's "Handbuch." The situation is complicated by the data appearing in the literature concerning the two phenols in dispute. The methods of synthesis of *p*-tertiary-butylphenol leave but little doubt as to its structure.[6]

Senkowski and earlier workers[7] have reported the synthesis of *p*-isobutylphenol from the action of zinc chloride on isobutyl alcohol and phenol. The product so prepared has physical constants almost identical with those of the tertiary derivative. Senkowski notes this. Evidence of this communication, and earlier ones, indicates that the isobutylphenol has never been prepared, the product being tertiary-butylphenol.

The experimental evidence of the present communication indicates that both tertiary and isobutyl phenyl ether isomerize to the same product, *p*-tertiary-butylphenol. This is an agreement with the experimental results of the previous workers but not with their conclusions. The present findings support the mechanism of Kraenzlein. The fact that isobutyl phenyl ether leads to a tertiary-butylphenol strongly indicates the need of a mechanism involving scission of the ether with readdition of the subsequent products. The apparent necessity for such a mechanism in this one case does not prove that all such reactions are not intramolecular, as it is conceivable that a compound may change to an isomer, with a decrease in free energy, by more than one path. The mechanism of these isomerizations is at present under further study.

Secondary-butyl phenyl ether was found to rearrange to *p*-secondary-butylphenol, which has been previously prepared.[8]

The behavior of tertiary-butyl phenyl ether is worthy of note. This compound isomerizes very readily to *p*-tertiary-butylphenol by the application of heat alone. It cannot be distilled at atmospheric pressure without rearrangement taking place. The pyrolysis of this ether is described.

Experimental

Preparation of the Ethers.—The phenyl ethers were prepared by the action of the alkyl bromides on a solution of sodium phenolate in alcohol. An equivalent of sodium

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(6) Studer, *Ber.*, **14**, 1474 (1881); *Ann.*, **211**, 242 (1882); Senkowski, *Ber.*, **23**, 2418 (1890); Gurewitsch, *ibid.*, **28**, 2428 (1895); Lewis, *J. Chem. Soc.*, **83**, 329 (1903).

(7) Senkowski, *Ber.*, **24**, 2974 (1891); Liebmann, *ibid.*, **14**, 1842 (1881); **15**, 150 (1882).

(8) Estreicher, *ibid.*, **33**, 442 (1900).

was added to excess alcohol; an equivalent of phenol was added to the clear solution so obtained. An excess of the alkyl halide was then added and the whole refluxed for six to eight hours. In the case of the tertiary butyl derivative the time of refluxing was shortened to twenty minutes to minimize isomerization. The excess alcohol and alkyl halide were removed by evaporation, the sodium bromide was washed out with water, the phenolic compounds were removed with 15% sodium hydroxide solution, and the remaining organic material was water-washed, dried and distilled. The yields of the isobutyl and secondary butyl ethers ranged from 80–90%. The yields of the tertiary-butyl phenyl ether were poor. The analytical data and physical properties of these compounds appear in Table I. The tertiary-butyl product was obtained as long white needles insoluble in 15% potassium hydroxide, and with no action on aqueous or alcoholic ferric chloride. The product was recrystallized from benzene. The pure recrystallized product melted under water. Due to rearrangement to the phenol, no accurate melting point could be determined. Prolonged heating in the melting point tube gave the melting point of the *p*-tertiary-butylphenol.

Catalytic Rearrangement of the Ethers.—Each ether was rearranged to the phenol by allowing it to stand a few days at room temperature with an equal weight of aluminum chloride. The catalyst was always added to the ether in small portions with external cooling. The aluminum chloride in each case dissolved in the ether with the formation of a viscous dark red mass. After standing, the products were decomposed with ice, water and hydrochloric acid. The organic products were separated, water-washed and extracted with 15% potassium hydroxide. The quantity of unrearranged ether was always very small. The alkaline solutions were neutralized with hydrochloric acid. The product from secondary-butyl phenyl ether was a liquid which was purified by distillation. The other two ethers yielded solid products which were purified by recrystallizations from water. Long white needles of the same melting point and the same mixed melting point were obtained. Yields were always in excess of 50%.

Pyrolytic Rearrangement.—The secondary and isobutyl phenyl ethers did not rearrange on ten hours of refluxing. Tertiary-butyl phenyl ether isomerized entirely to an alkali-soluble product on a few hours of refluxing. The boiling point rose from 192 to 230° in three hours. The product was recrystallized from water. The mixed melting points with the products obtained by catalytic ether rearrangement were identical.

TABLE I

BUTYL PHENYL ETHERS AND BUTYLPHENOLS

Sec-butyl phenyl ether has been rearranged to the phenol by means of a sulfuric–acetic acid rearranging mixture by Natelson (Ph.D. Thesis, N. Y. U., 1931) and Siegel (M.Sc. Thesis, N. Y. U., 1933). The product they obtained is the same as that reported here.

Phenyl ethers	Ref. index n_D^{24}	Density	B. p., °C.	Formula	Analyses, % Carbon	Analyses, % Hydrogen
				Calcd.:	80.0	9.3
(a) Isobutyl	1.4932	d^{24} 0.924	196	$C_6H_5OCH_2CH(CH_3)_2$	80.4	9.4
(b) *Sec*-butyl	1.4943	d^{21} .973	193	$C_6H_5OCH(CH_3)(C_2H_5)$	80.7	9.2
					80.1	9.8
(c) Tert-butyl	....	......	192	$C_6H_5OC(CH_3)_3$	79.9	9.8
P-sec-butylphenol	1.5182	d^{21} .986	236	$HOC_6H_4CH(C_2H_5)(CH_3)$	80.2	9.3
p-Tert-butylphenol						
(a) By the action of heat on *t*-butylphenol ether	....	......	230 (m. p. 100)	$HOC_6H_4C(CH_3)_3$	79.6	9.5
(b) By catalytic rearrangement of *t*-butyl phenyl ether	....	......	230 (m. p. 100)	$HOC_6H_4C(CH_3)_3$	79.4	9.4
(c) By catalytic rearrangement of isobutyl phenyl ether	....	......	230 (m. p. 100)	$HOC_6H_4C(CH_3)_3$	79.3	9.7

The author wishes to acknowledge his indebtedness to Miss R. T. Roth for the analyses performed.

Summary

1. Iso, secondary and tertiary-butyl phenyl ethers have been prepared and catalytically rearranged to phenolic compounds.

2. The rearrangement of tertiary-butyl phenyl ether by the action of heat has been described.

NEW YORK, N. Y.

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PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Studies on the Rearrangement of Tertiary-butylmethylcarbinol (Pinacolyl Alcohol). II.[1] Dehydration

BY FRANK C. WHITMORE AND P. L. MEUNIER[2]

A primary alcohol containing the grouping R_3CCH_2OH can be dehydrated only with rearrangement.[3] On the other hand, a related tertiary alcohol, $R_3CC(OH)R_2$, is dehydrated mainly without rearrangement.[4] Conceivably a secondary alcohol, $R_3CCHOHR$, could be dehydrated either with or without rearrangement.[5] Until the present study, only rearranged products had been reported from the dehydration of such secondary alcohols.[1,6] The simplest of these alcohols, tertiaryl-butylmethylcarbinol, has been dehydrated by many workers.[7] The products obtained have been rearranged olefins, tetramethylethylene (b. p. 72°), and *unsym*-methylisopropylethylene (b. p. 54°). Previous work in this Laboratory has shown that the intermediate fraction, b. p. 65–67°, observed by some workers, is a mixture of the same two olefins.[1] The only preparations of the normal dehydration product, *tert*-butylethylene, have been made indirectly by the thermal decomposition of the xanthate of pinacolyl alcohol[8] and of the acetate.[1]

In the present work the pinacolyl alcohol was purified by repeated distillation and fractional crystallization and a large quantity was dehydrated at high pressure and temperature over a catalyst of phosphoric acid on silica gel. The usual rearranged olefins, tetramethylethylene and *unsym*-methylisopropylethylene, were obtained but, in addition, a small

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(1) Whitmore and Rothrock, THIS JOURNAL, 55, 1106 (1933).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Whitmore and Rothrock, THIS JOURNAL, 54, 3431 (1932); Whitmore and Church, *ibid.*, 55, 1119 (1933).

(4) Whitmore and Laughlin, *ibid.*, 54, 4011 (1932).

(5) Whitmore, *ibid.*, 54, 3274 (1932).

(6) Whitmore and Houk, *ibid.*, 54, 3714 (1932); Whitmore and Krueger, *ibid.*, 55, 1528 (1933).

(7) See citations to literature in Ref. 1.

(8) Fomin and Sochanski, *Ber.*, 46, 244 (1913).

amount (3%) of the unrearranged olefin, *tert*-butylethylene, was isolated and identified.

Experimental

Preparation and Purification of Tert-butylmethylcarbinol.—The alcohol, b. p. 118.7–119.7 (741 mm.), 120.4° (760 mm.), n^{20}_{D} 1.4148, was prepared by the action of acetaldehyde on *tert*-butylmagnesium chloride.[1] The yield for a 20-mole run, based on the chloride used, was 52.1%. The alcohol was distilled in an efficient laboratory column, 125 × 2.3 cm.,[9] after which it was further purified by fractional crystallization. In this way the freezing point was raised from 1.5 to 5.3°.

Dehydration of Tert-butylmethylcarbinol.—Ordinary laboratory methods for dehydrating the alcohol, using sulfuric acid, orthophosphoric acid, phosphoric anhydride, and oxalic acid, proved unsatisfactory for dehydrating large quantities. Finally, the alcohol was dehydrated in a high pressure flow system containing an electrically heated high pressure reactor made of Shelby seamless tubing, 91 cm. by 1.6 cm. (inside), partly filled with a catalyst of phosphoric acid on silica gel. A pump, adapted for handling small quantities of liquid, was used to pump the alcohol through the system. In a typical run 500 g. of the alcohol was dehydrated at 300° and 2500 lb. pressure. The loss was only 2%. The yield of olefins was 337 g. or 80%. These were repeatedly fractionated in a partial condensation column, 90 × 1.2 cm., using a reflux ratio of 200:1.[9] This gave three fractions of boiling range (740 mm.), wt., yield and n^{20}_{D} as follows: 38–43°, 10.5 g., 3%, 1.3775; 54–58°, 107 g., 31%, 1.3904; 69–72°, 208 g., 61%, 1.4121. The last two fractions were *unsym*-methylisopropylethylene and tetramethylethylene, respectively. The low-boiling fraction was identified as *tert*-butylethylene by ozonolysis.[10] In the aqueous layer of the decomposition products of the ozonide, qualitative tests for formaldehyde were obtained with fuchsin reagent and with aqueous resorcinol. The oily product oxidized in air to trimethylacetic acid, which was identified by conversion to the amide, m. p. 145–148°. Mixed with pure trimethylacetamide (m. p. 153–154°), it melted at 149–151°.

Summary

The catalytic dehydration of *tert*-butylmethylcarbinol at high temperature and pressure gave the rearranged olefins, tetramethylethylene and *unsym*-methylisopropylethylene, in the ratio 2:1 and, in addition, a small amount of the normal dehydration product, tertiary-butylethylene.

STATE COLLEGE, PENNSYLVANIA

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[9] Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

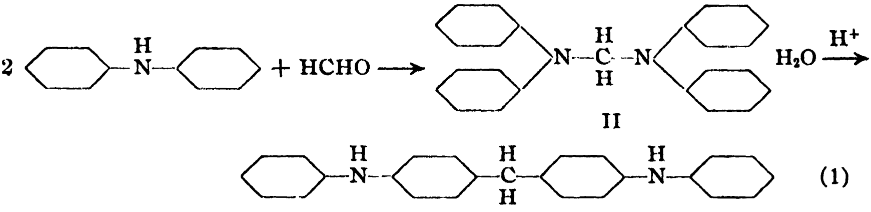
[10] Whitmore and Church, *ibid.*, **54**, 3712 (1932).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE B. F. GOODRICH CO.]

The Reaction of Formaldehyde with Diphenylamine

BY DAVID CRAIG

The formation of dianilinodiphenylmethane as a product of the reaction of formaldehyde with diphenylamine[1,2] has long been claimed. However, the isolation of pure compounds from the products of the reaction has not been recorded up to this time. This is true notwithstanding the fact that Straus and Bormann[3] succeeded in preparing *p,p'*-dianilinodiphenylmethane in a series of reactions starting with *p,p'*-diaminodiphenylmethane. A study of the reaction of formaldehyde with diphenylamine[4] under a variety of conditions was therefore undertaken, the results of which are described in this communication.



I (1)

The course of the reaction of formaldehyde with diphenylamine in the presence of acids is dependent on the relative amounts of the reactants used. An excess of diphenylamine favors the formation of *p,p'*-dianilinodiphenylmethane. On the other hand, if an excess of formaldehyde or even equimolecular amounts of the reactants are employed, resins are formed which hinder or prevent the isolation of a pure product. Possibly these resins result from subsequent condensation with formaldehyde to form long chain molecules of the Staudinger type. This condensation occurs readily in the absence or presence of acid catalysts. Resins may also be obtained directly from *p,p'*-dianilinodiphenylmethane by heating with strong acids, diphenylamine being formed as one of the products.[5] Indeed, it appears that resins of this type are the ultimate condensation products of formaldehyde with amines rather than the simple diphenylmethanes as suggested by Wagner.[6]

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(1) Meister, Lucius and Brüning, German Patent 58,072, June 24, 1891; *Friedländer*, **3**, 79 (1890–1894). See also Kostyschew, *Ber.*, **45**, 1291 (1912).

(2) Sen and Sen, *J. Indian Chem. Soc.*, **7**, 965 (1930).

(3) Straus and Bormann, *Ber.*, **43**, 729 (1910).

(4) Reaction products of formaldehyde with diphenylamine have recently been patented as antioxidants for rubber. (a) Clifford, U. S. Patent 1,849,822, March 15, 1932; (b) Clifford, U. S. Patent 1,763,579, June 10, 1930; (c) Semon, U. S. Patent 1,860,434, May 31, 1932; (d) Semon, U. S. Patent 1,890,916, Dec. 13, 1932.

(5) In this connection see von Braun, "The Thermal and Hydrolytic Decomposition of Amino and Hydroxy Diarylmethanes," *Ann.*, **472**, 1–89 (1929).

(6) Wagner, THIS JOURNAL, **55**, 724 (1933).

The structure of the *p,p'*-dianilinodiphenylmethane is established by reference to the properties reported by Straus and Bormann[3] and also by synthesizing the compound by the method of Ullmann[7] from *o*-chlorobenzoic acid and *p,p'*-diaminodiphenylmethane.

The formation of *p,p'*-dianilinodiphenylmethane from diphenylamine and formaldehyde probably takes place in more than one step. If no acid catalyst is used and the reaction is carried out in benzene solution, there may be isolated as the chief product a compound (Compound II) having the empirical formula and molecular weight of tetraphenylmethylenediamine.

Compound II is rapidly hydrolyzed by warm, dilute mineral acids to formaldehyde and diphenylamine. It rearranges in the presence of diphenylamine and hydrochloric acid to *p,p'*-dianilinodiphenylmethane in a manner characteristic of other arylmethylenediamines.[8] In the absence of added diphenylamine and in the presence of dry hydrogen chloride, resinification occurs with the splitting out of diphenylamine but without the formation of *p,p'*-dianilinodiphenylmethane. The hydrogenolysis of Compound II in the presence of the Adkins copper chromite catalyst occurs with the formation of diphenylamine and methyldiphenylamine. No phenyl-*p*-tolylamine is formed. However, a side reaction taking place during this reduction is the rearrangement to form *p,p'*-dianilinodiphenylmethane. This, together with the fact that greater amounts of diphenylamine are formed during the reduction than can be accounted for by simple hydrogenolysis, indicates that Compound II has a tendency to dissociate with the formation of free methylene $\mathrm{H}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$. It should be pointed out that methyldiphenylamine does not undergo reduction under the conditions found suitable for rapidly reducing Compound II.

The mode of formation and the reactions of Compound II indicate that it is tetraphenylmethylenediamine. It is interesting that Houben and Arnold[9] reported the formation of this substance as a product of the reaction of chloromethyl sulfate with diphenylamine. The product which they obtained readily hydrolyzed to formaldehyde and diphenylamine; however, it melted at 82–85°, while the tetraphenylmethylenediamine here reported melts at 104–105°. It is, therefore, believed that Houben and Arnold's compound was impure and probably contaminated with *p,p'*-dianilinodiphenylmethane. Houben and Arnold did not mention the previous crude preparation of tetraphenylmethylenediamine from the reaction of formaldehyde with diphenylamine.[10]

In searches for precursors of tetraphenylmethylenediamine it has not thus far been possible to isolate an amino alcohol,[8,11] an anhydroamino

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(7) Ullmann, *Ann.*, **355**, 325 (1907).

(8) Morgan, *J. Soc. Chem. Ind.*, **49**, 245 (1930).

(9) Houben and Arnold, *Ber.*, **41**, 1577 (1908).

(10) German Patent 158,718, January 23, 1905; *Friedländer*, **8**, 402 (1905–1907).

(11) German Patent 97,710, November 21, 1898; *Friedlander*, **5**, 95 (1897–1900).

alcohol, or a polymer thereof from mixtures secured from the reactions of formaldehyde with diphenylamine.

Experimental

The Reaction of Formaldehyde with Diphenylamine to Form *p,p'*-Dianilinodiphenylmethane, I.—This reaction was carried out by adding 1 cc. of concentrated hydrochloric acid to a mixture of 254 g. (1.5 moles) of diphenylamine and 16 g. (0.19 mole) of 36% formaldehyde dissolved in 250 cc. of alcohol at 40°. Reaction set in immediately and was complete after refluxing for thirty minutes on the steam-bath. Four grams of potassium carbonate was added and the product isolated by distillation in a 500-cc. Anders flask. The diphenylamine distilled off had a setting point of 53° and amounted to 192 g. The intermediate fraction amounting to 2.5 g. came over below 270° at 1.5 mm. of mercury and consisted mainly of *p,p*-dianilinodiphenylmethane. The main fraction distilled with considerable superheating between 270 and 290° at the same pressure. The yield of this fraction amounted to 41.5 g. or to a yield of 63% of crude product calculated on the formaldehyde used. When recrystallized from 250 cc. of alcohol, 35 g. of *p,p'*-dianilinodiphenylmethane was obtained having a melting point of 114–115°. After melting, the compound resolidified and melted at 120°. On recrystallization the second melting point was raised to 122–123°, the initial melting point being at 118–120°. The residue from the distillation weighed 23 g.

Anal. Calcd. for $C_{25}H_{22}N_2$: C, 85.7; H, 6.32; N, 7.98. Found: C, 85.7; H, 6.13; N, 8.06.

Solvents such as benzene, acetone, gasoline, and acetic acid were used for this reaction and found suitable. If acetic acid was used as the solvent, hydrochloric acid was not necessary as the catalyst. The reaction may be carried out in the absence of a solvent if an efficient agitator is used.

Difficulties encountered by previous workers who may have tried to isolate this compound are partly due to the fact that they did not use sufficient diphenylamine in the reaction. Using the amounts of the reactants called for by Equation (1) drops the yield to about 40%.

Under the proper conditions formaldehyde may be replaced by other methylene compounds. Anhydroformaldehyde aniline, hexamethylenetetramine, and diaminodiphenylmethane reacted above 150° with an excess of diphenylamine to form *p,p'*-dianilinodiphenylmethane. Chloromethyl ether in benzene solution reacted as vigorously as formaldehyde with diphenylamine, *p,p'*-dianilinodiphenylmethane being the main product. In order to carry out the reaction with paraformaldehyde, water was added and the mixture refluxed for several hours.

A double melting point for *p,p'*-dianilinodiphenylmethane was also observed by Straus and Bormann.[3] It was frequently found, however, that only the high melting form was obtained.

The Synthesis of *p,p'*-Dianilinodiphenylmethane by the Ullmann Method.—Fifteen grams of *o*-chlorobenzoic acid, 15 g. of potassium carbonate, and 10 g. of *p,p'*-diaminodiphenylmethane were intimately mixed in a 500-cc. flask and heated to 150° with stirring in an oil-bath. A trace of cuprous iodide was added, whereupon a vigorous reaction set in. The mixture turned black and considerable foaming occurred. After a few minutes the product was cooled and dissolved in 500 cc. of water. The solution was acidified with acetic acid, which precipitated an oily solid. This oily solid, which was a mixture of *o*-chlorobenzoic acid with anthranilic acids, was separated and heated to 250° for a few minutes with stirring. Carbon dioxide was evolved. The resulting product was then extracted with 100 cc. of 10% sodium hydroxide and the insoluble part was distilled. Two grams of a fraction boiling at about 280° at 1.5 mm.

was obtained, which on being recrystallized from alcohol melted at 121° and did not depress the melting point of the material melting at 122–123° secured from formaldehyde and diphenylamine.

The Preparation of Tetraphenylmethylenediamine, II.—One hundred and sixty-eight grams (2 moles) of 36% formaldehyde was added during two hours to a refluxing solution of 338 g. (2 moles) of diphenylamine in 250 cc. of benzene. Refluxing was continued for forty-five minutes. When the product was distilled, 87 g. of impure diphenylamine came over first. The next fraction boiling between 200 and 240° at 2.5 mm. pressure of mercury weighed 244 g. This represents a conversion of 70% based on the diphenylamine used. By redistillation and crystallization about two-thirds of this material was isolated as the pure compound melting at 104–105°. On dissolving the crude product in an equal volume of benzene and then stirring in two volumes of petroleum ether, thick transparent crystals were obtained. The compound was difficultly soluble in hot alcohol, from which it crystallized readily.

Anal. Calcd. for $C_{25}H_{22}N_2$: C, 85.7; H, 6.32; N, 7.98. Found: C, 85.1; H, 6.32; N, 7.98. *Mol. wt.* (in freezing benzene). Calcd. for $C_{25}H_{22}N_2$: 350. Found: 326, 329.

When warmed with very dilute hydrochloric acid or with 10% sulfuric acid, formaldehyde and diphenylamine were obtained. It also reacted with potassium bisulfite[10] solution, although the products of this reaction were not isolated.

The Rearrangement of Tetraphenylmethylenediamine into *p,p'*-Dianilinodiphenylmethane.—When 35 g. (0.1 mole) of the compound prepared by the above described method and melting at 103–105° was mixed with 33.8 g. (0.2 mole) of diphenylamine dissolved in 130 cc. of alcohol no reaction took place, but when 0.9 cc. of concentrated hydrochloric acid was added the temperature rose from 45 to 55° and an oil separated out which on standing overnight gave a small amount of crystals which was filtered off and washed with alcohol. After recrystallizing from alcohol the crystals melted at 148–152°. These crystals were not identified. The same material was secured from high boiling fractions of formaldehyde-diphenylamine reaction products. The alcoholic washings were united with the main solution and two volumes of water and 5 g. of sodium carbonate was added. The oil obtained was distilled in the usual way and gave as the main product *p,p'*-dianilinodiphenylmethane. After recrystallizing from alcohol the product melted at 122–123° when alone or when mixed with the *p,p'*-dianilinodiphenylmethane prepared directly from formaldehyde and diphenylamine.

The Hydrogenolysis of Tetraphenylmethylenediamine.—This reaction did not occur with sodium and alcohol but was successfully carried out by the method of Adkins. One hundred and seventeen grams (0.33 mole) of tetraphenylmethylenediamine, 250 cc. of benzene, and 4 g. of the copper chromite catalyst were placed in the reducer. Hydrogen at about 110 atmospheres pressure was admitted and the temperature raised to 225° gradually during four hours. The mixture was filtered and distilled at reduced pressure. Diphenylamine amounting to 63 g. or 0.37 mole, about 5 g. of methyldiphenylamine, and a trace of *p,p'*-dianilinodiphenylmethane were isolated from the product, besides about 30 g. of resinous material. The diphenylamine and methyldiphenylamine were separated from each other by the method described by Gibson and Vining.[12] The *p,p'*-dianilinodiphenylamine was isolated as described above. This compound and the diphenylamine were identified by melting points and mixed melting points with authentic specimens. The methyldiphenylamine was identified by the melting point and mixed melting point of its zinci-hydrochloride with an authentic specimen of this derivative, the preparation of which is described in the next section.

Under the conditions just described for the hydrogenolysis of tetraphenylmethylenediamine no reaction with 38 g. of methyldiphenylamine, 2 g. of copper chromite and 100 cc. of benzene could be detected.

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[12] Gibson and Vining, *J. Chem. Soc.*, **123**, 834 (1923).

The Zinci-hydrochloride of Methyldiphenylamine.—Five grams (0.027 mole) of redistilled methyldiphenylamine obtained from the Eastman Kodak Company was dissolved in 40 cc. of glacial acetic acid. A solution of 5 g. of zinc chloride dissolved in a mixture of 5 cc. of concd. hydrochloric acid and 10 cc. of glacial acetic acid was added. A precipitate came down immediately. After cooling to 15° for fifteen minutes the precipitate was filtered off and washed consecutively with 20 and 10 cc. portions of glacial acetic acid. After standing in a vacuum desiccator to constant weight over potassium hydroxide a yield of 7.5 g. (95%) of a white powder was obtained, m. p. 186–188°, with evolution of hydrochloric acid. The compound can also be prepared in concentrated hydrochloric acid, in which it is difficultly soluble.

Anal. Calcd. for $[(C_6H_5)_2NCH_3 \cdot HCl]_2 \cdot ZnCl_2$: Zn, 11.4. Found: Zn, 11.4, 11.8. Calcd. for $[(C_6H_5)_2NCH_3 \cdot HCl]_2 \cdot ZnCl_2$, equiv. wt.: 143.5 according to the equation $[(C_6H_5)_2NCH_3 \cdot HCl]_2 \cdot ZnCl_2 + 4NaOH\ 2(C_6H_5)_2NCH_3 + Zn(OH)_2 + 4NaCl + 2H_2O$. Found by titrating with 0.01 N NaOH using phenolphthalein as the indicator: 140, 141.

This compound is hydrolyzed to methyldiphenylamine, zinc chloride and hydrochloric acid when mixed with water but is not particularly hygroscopic. Mixtures with water were titrated with standard potassium ferrocyanide solution for the zinc analysis and with standard sodium hydroxide solution for the equivalent weight determination without removing the precipitated methyldiphenylamine. During the titration with sodium hydroxide a precipitate of zinc hydroxide came down.

The author is grateful to Dr. W. L. Semon, under whose direction this work was conducted.

Summary

The main reaction product of formaldehyde with an excess of diphenylamine in the presence of hydrochloric acid has been found to be *p,p'*-dianilinodiphenylmethane. A possible intermediate product has been identified as tetraphenylmethylenediamine.

AKRON, OHIO

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[Contribution from the Department of Chemistry, University of Notre Dame]

Mono and Disubstituted Organo-Mercury Derivatives of Acetylene

By R. J. Spahr, R. R. Vogt and J. A. Nieuwland

We have recently reported[1] the preparation and properties of a series of aryl and normal alkyl mercury acetylides formed by the replacement of both atoms of hydrogen from acetylene by organo-mercury groups. The present paper describes the similar preparation and some variations in the behavior of analogous compounds containing branched alkyl and a few substituted alkyl and aryl groups linked to mercury.

In the preparation of acetylides containing secondary organo-mercury radicals and also of bis-amylmercury acetylide it was noticed after these compounds had been precipitated from alcoholic potassium hydroxide solution, that they could be redissolved by excess acetylene. When the excess acetylene was allowed to escape or was removed by suction, a precipitate separated from solution. In each case comparison of the melting points of purified samples of the two precipitates proved them to be identical, and analysis showed that both hydrogens of acetylene had been replaced by organo-mercury groups.

These acetylides were all very soluble in the common organic solvents, and greater solubility was found to be associated with a more rapid reaction with excess acetylene. It was also found that the more soluble of the normal alkyl mercury acetylides were very slowly redissolved. So it appears that this phenomenon is not due to the presence of any one type of group, but depends solely on the solubility of the bis-organomercury acetylide.

It was found that the presence of alkali in solution catalyzed the formation of the acetylides and their solution in excess acetylene. Thus four minutes elapsed before a precipitate began to appear when acetylene was passed into an alkali-free alcoholic solution of ethylmercury hydroxide prepared by the action of silver hydroxide on ethylmercury chloride in alcohol.[2] An alcoholic potassium hydroxide solution, having the same concentration of ethylmercury chloride, gave the acetylide precipitate immediately. Likewise when the purified acetylides were suspended in alcohol they were slowly attacked by acetylene, while the addition of sodium or potassium hydroxide or even ammonia to these solutions caused the acetylene to dissolve the precipitates much more rapidly.

In order to explain these facts it was assumed that an equilibrium exists between the mono and the bis-organo-mercury acetylides $C_2H_2 + R{-}Hg{-}C{\equiv}C{-}Hg{-}R \rightleftarrows 2\,R{-}Hg{-}C{\equiv}C{-}H$.

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(1) Spahr, Vogt and Nieuwland, This Journal, 55, 2465 (1933).

(2) Dunhaupt, *J. prakt. Chem.*, [1] 61, 415 (1854).

The catalytic effect of the alkali may possibly be explained as being due to the existence of more acetylide ions in alkaline solution. It has not as yet been found possible to isolate compounds of the type R—Hg—C≡C—H, but their mode of formation and certain reactions indicate their presence in solution. A reaction of this type is the preparation of isopropylmercury *n*-amyl acetylide formed by the action of *n*-amylacetylene on bis-isopropylmercury acetylide in the presence of excess acetylene.

Marvel and Gould have pointed out[3] that the carbon–mercury linkage R_2CH—Hg— is more easily broken than that in R—CH_2—Hg— by heat and acids. We have found that the same relationship holds with regard to stability toward aqueous alkaline solution. When a secondary organomercury acetylide was prepared in aqueous alkaline solution, it decomposed, splitting out metallic mercury and leaving a black gummy mass from which no crystalline precipitate could be obtained. In an alcoholic alkaline solution prepared from absolute alcohol, the acetylide is stable.

Schoeller and Schrauth[4] have called attention to the fact that α-acetoxymercuri-β-methoxyethane is a powerful vesicant, producing irritating blisters when in contact with the skin. The acetylide of this compound when applied to the skin in undiluted form produced no skin irritation. When heated above its melting point it decomposed, metallic mercury splitting out, leaving behind an oil with a carnation-like odor which solidified on cooling to room temperature. The products of this reaction are at present being investigated.

Experimental Part

Preparation of Organomercury Bromides.—The secondary alkyl mercury, isoamylmercury, and cyclohexylmercury bromides were prepared by converting the organobromide into its Grignard compound, and treating this with an excess of mercuric bromide.[5]

Preparation of *p*-Aminophenylmercury Chloride.—Freshly distilled aniline was treated with mercuric acetate and the *p*-aminophenylmercury acetate which formed was finely powdered and boiled with a large volume of water containing an excess of sodium chloride. Shiny leaflets of *p*-aminophenylmercury chloride separated from solution on cooling.[6]

Preparation of *o*-Nitrophenylmercury Chloride.—Mercuric acetate was heated with five times its weight of nitrobenzene until the solution no longer gave a test with sodium hydroxide. It was allowed to cool and filtered. The filtrate was treated with an excess of sodium chloride solution and steam distilled to remove any unreacted nitrobenzene. The residue was dried and extracted with ligroin, and recrystallized from glacial acetic acid. It was soluble in ether and high boiling ligroin and insoluble in water, m. p. 180–182.°[6]

Preparation of *o*-Hydroxyphenylmercury Chloride.—This was prepared from phenol, mercuric acetate and sodium chloride according to the method of Whitmore and Hanson.[7]

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[3] Marvel and Gould, THIS JOURNAL, **45**, 820–823 (1923).

[4] Schoeller and Schrauth, *Ber.*, **46**, 2869 (1913).

[5] Marvel and Calvery, THIS JOURNAL, **45**, 820–823 (1923); Hill, *ibid.*, **50**, 167 (1928); Grüttner, *Ber.*, **47**, 1651–1656 (1914).

[6] Dimroth, *ibid.*, **35**, 2032–2045 (1902).

Preparation of Allylmercury Iodide.—This was prepared by the method of Zinin from allyl iodide and metallic mercury.[8]

Preparation of α-Acetoxymercuri-β-methoxyethane.—It was prepared according to the method of Schoeller and Schrauth,[4] as modified by Manchot,[9] and further modified by Ford in this Laboratory.[10]

Ethylene was passed into a solution of one-half mol of mercuric acetate in excess alcohol and one-half mol of mercuric oxide was added at a rate which kept the reaction mixture a faint pink. A Benning gas absorption stirrer[11] was used and the reaction was conducted in a three-necked water-cooled flask, ethylene being supplied by the constant pressure, alarm, gas feeding device described by Vaughn.[12] The reaction was complete in one-quarter hour. After removing the alcohol *in vacuo*, the residue was recrystallized from ether. The melting point was 42°. The yield based on total mercury used was 92.8%.

Preparation of Mercury Acetylides. General Procedure.—They were prepared according to the method outlined in a previous communication,[1] except that a 10% alcoholic solution of potassium hydroxide was used instead of an aqueous solution. The secondary alkyl mercury and the isoamylmercury acetylides were very soluble in the common organic solvents, and were crystallized from ethyl alcohol, giving in each case fine needles. Their melting points are recorded in Table I. The *o*-nitrophenylmercury acetylide is practically insoluble in all organic solvents, and we were unable to purify it by crystallization. Its melting point could not be determined for on heating it above 300°, it decomposed with explosive violence. The *p*-aminophenylmercury acetylide is but slightly soluble in organic solvents. It crystallized in long needles from ethyl alcohol, and turned brown when exposed to the air. Allylmercury iodide, when dissolved in alcoholic ammonia and treated with acetylene, gave a white precipitate which immediately decomposed on exposure to air liberating black metallic mercury.

Table I

Mercuric Acetylides, General Formula $R—Hg—C≡C—Hg—R$

Nature of R	M. p., °C.	Mercury, % Calcd.	Mercury, % Found
Isopropyl	110.5–111.5	78.46	78.18
Sec-butyl	105.5–106	74.38	74.25
Isoamyl	106 –107	70.70	70.72
Cyclohexyl	172 –173	67.84	67.51
β-Methoxyethyl	129.5–130.5 (with dec.)	73.85	73.41
p-Aminophenyl	188 –190 (with dec.)	65.65	66.34
o-Nitrophenyl	Explodes above 300°	59.94	60.99

Method of Analysis.—Mercury was determined according to the method outlined in a previous communication.[1]

Attempted Preparation of *o*-Hydroxyphenylmercury Acetylide.—No acetylide was obtained on passing acetylene into either *o*-hydroxyphenylmercury chloride in alcoholic potash or *o*-hydroxyphenylmercury hydroxide in alcohol. In the latter solution the

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(7) Whitmore and Hanson, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. IV, 1925, p. 13.

(8) Zinin, *Ann.*, **96**, 353 (1855).

(9) Manchot, *Ber.*, **53**, 986 (1920).

(10) Ford, Thesis, University of Notre Dame, 1933.

(11) Benning, *Proc. Ind. Acad. Sci.*, **37**, 263 (1927).

(12) Vaughn, *J. Chem. Educ.*, **9**, 528 (1932).

final products appeared to be free mercury and phenol which was identified by conversion into picric acid. It is possible that these were formed by the decomposition of an intermediate acetylide.

Preparation of Isopropylmercury Amyl Acetylide.—12.5 g. of isopropylmercury bromide was dissolved in a 10% alcoholic potassium hydroxide solution. Four grams of amylacetylene was added slowly to the isopropylmercury hydroxide which was mechanically stirred. During the addition, the solution assumed a pale yellow color. On the addition of 300 ml. of water to the stirred solution an oil separated and settled to the bottom of the flask. The oil was separated and dried over anhydrous sodium sulfate. It contained a trace of amylacetylene which was removed by distillation under reduced pressure. The crude product weighed 9.2 g. (70% yield). It is an oil with a pale yellow color and of very penetrating odor. It is insoluble in water, but miscible with organic solvents. This material could not be distilled even under 3 cm. pressure on account of decomposition with the formation of free mercury, d_4^{20} 1.628.

Anal. Calcd.: Hg, 59.22. Found: Hg, 58.59.

Acknowledgment.—The authors wish to thank Mr. Joseph Pozzi, who kindly prepared the secondary organo-mercury halides.

Summary

1. The acetylene derivatives of isopropyl, *sec*-butyl, isoamyl, cyclohexyl, *o*-nitrophenyl, *p*-aminophenylmercury halides and α-acetoxymercuri-β-methoxyethane have been prepared and their properties recorded.

2. Isopropylmercury amyl acetylide has been prepared and its properties are recorded.

3. It has been shown that alkalies act as catalyst in the formation of organo-mercury acetylides.

4. Evidence of the existence of mono-mercury acetylides in solution has been given, and it has been shown that the formation of such compounds from the di-mercury acetylides when treated with excess acetylene depends primarily upon the solubility of the di-mercury derivative.

5. Secondary organo-mercury acetylides are unstable in aqueous potassium hydroxide solution, undergoing decomposition with the liberation of mercury.

NOTRE DAME, INDIANA

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Dehydration of Tertiary Alcohols Containing a Neopentyl System. II.[1] Methylisopropyl-*tert*-butylcarbinol, Methyldi-*tert*-butylcarbinol, and Methylethylneopentylcarbinol

BY FRANK C. WHITMORE AND KENNETH C. LAUGHLIN[2]

The three alcohols, methylisopropyl-*tert*-butylcarbinol, methyldi-*tert*-butylcarbinol, and methylethylneopentylcarbinol, were selected as representing various types of tertiary alcohols containing a neopentyl group. The study of the dehydration of methylethyl-*tert*-butylcarbinol and dimethyl-*tert*-amylcarbinol has been continued.[1]

Dehydration of methylethyl-*tert*-butylcarbinol with β-naphthalenesulfonic acid gave the same mixture of olefins as with iodine.[1] Ozonolysis of intermediate fractions failed to give positive evidence for any olefin formed by dehydration from the methyl group. Dehydration of dimethyl-*tert*-amylcarbinol gave less than 6% of 2,2,3-trimethylpentene-3 formed by rearrangement of a methyl group.[1] The rearrangement of the ethyl group would give the same olefin as would the normal dehydration.[1,3]

Methylisopropyl-*tert*-butylcarbinol gave 3,3-dimethyl-2-isopropylbutene-1 (by normal dehydration involving the methyl group) and the rearrangement product 2,3,3,4-tetramethylpentene-1 in the ratio 3 : 1, with only traces of 2,3,4,4-tetramethylpentene-2 (by normal dehydration involving the isopropyl group). The sluggishness of the isopropyl group in losing a proton is noteworthy and is being further studied.[4] Methyldi-*tert*-butylcarbinol gave over 90% of 2-*tert*-butyl-3,3-dimethylbutene-1 (by dehydration involving the methyl group), and some low-boiling material which has not been identified. Methylethylneopentylcarbinol was dehydrated without rearrangement, giving mainly 2,2,4-trimethylhexene-4 (from the ethyl group), with less than 5% of 2,2,4-trimethylhexene-3 (from the neopentyl group) and only traces of 4,4-dimethyl-2-ethylpentene-1 (from the methyl group).

These results show the tendency of tertiary alcohols to dehydrate without rearrangement, in contrast to related primary and secondary alcohols containing a neopentyl group, which dehydrate mainly with rearrangement.[5]

With the hydroxyl group directly attached to the neopentyl system, the amount of rearrangement varied from less than 6% in the case of dimethyl-*tert*-amylcarbinol and methyldi-*tert*-butylcarbinol to 25% in the case of methylisopropyl-*tert*-butylcarbinol. No rearrangement was found when the hydroxyl group, as in methylethylneopentylcarbinol, was not attached to the neopentyl system.

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[1] Whitmore and Laughlin, THIS JOURNAL, **54**, 4011 (1932).

[2] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[3] Whitmore, THIS JOURNAL, **54**, 3276 (1932).

[4] Unpublished results, T. S. Oakwood of this Laboratory. *Cf.* Whitmore and Houk, *ibid.*, **54**, 3716 (1932); Whitmore and Evers, *ibid.*, **55**, 814 (1933).

[5] For references see Whitmore and Meunier, *ibid.*, **55**, 3721 (1933).

Experimental Part

Distillation Equipment.—The Johnston column has been described.[6] Column N[7] was of the same partial condensation type, but with a thermometer at the top of the packing so as to obtain significant temperature readings. The packed section, 130 × 1.4 cm., filled with 4-mm. glass helixes,[8] was equivalent to 16.5 theoretical plates.

Columns K, 44 × 1.4 cm., 9.6 theoretical plates, and L, 40 × 0.8 cm., 7.7 theoretical plates, were also packed with glass helixes. They were of the total condensation, variable take-off type previously described.[6] The 65 × 2.3 cm. column, and column A, 38 × 1.5 cm., were of the same type, but were packed with glass tubes (5 × 5 mm.). Column B, 25 × 0.8 cm., of the partial condensation indented type with no packing, was fitted with a 50-cc. pear-shaped flask by a ground-glass joint.

Preparation and Dehydration of Methylethyl-*tert*-butylcarbinol.—Methyl *tert*-butyl ketone (2 moles)[9] with 2.5 moles of ethylmagnesium bromide gave a 64% yield of methylethyl-*tert*-butylcarbinol, b. p. 76.1–76.6° (50 mm.), n^{20}_D 1.4354, d^{20}_4 0.849. The alcohol was dehydrated by distilling from 0.1 g. of β-naphthalene sulfonic acid through column K. The yield of olefin after drying and redistilling was 138 g. (95%). This was distilled through column N, the resulting curve showing the presence of 2,2,3-trimethylpentene-3 and 2,3,3-trimethylpentene-1 in the ratio 4:1 the same as with iodine as the dehydrating agent.[1] The following physical properties were determined:

	Cottrell b. p. °C., 760 mm.	n^{20}_D	d^{20}_4
2,2,3-Trimethylpentene-3	111.9	1.4232	0.739
2,3,3-Trimethylpentene-1	108.2	1.4178	0.736

In the search for some dehydration involving the methyl group, the intermediate fractions from two distillations (88 g.) were redistilled through column N without any indication of material with either a constant b. p. or refractive index. Since no third olefin could be separated by distillation, the intermediate fractions were again combined (73 g.) and ozonized as usual.[10] Formaldehyde was formed. The oily products were fractionated through column L, and the material of b. p. 116–126° (740 mm.) was treated with 2,4-dinitrophenylhydrazine. The main product was the derivative of methyl *tert*-amyl ketone (m. p. 111–111.5°). Careful fractional crystallization yielded no higher melting derivative. Thus no ethyl *tert*-butyl ketone (2,4-dinitrophenylhydrazone m. p. 145°[11]) was present, and consequently there was no dehydration from the methyl group.

Preparation and Dehydration of Dimethyl-*tert*-amylcarbinol.—Ethyl dimethylethylacetate, b. p. 140–140.8° (730 mm.), n^{20}_D 1.4040, was prepared in 37% yield from *tert*-amylmagnesium chloride and ethyl chlorocarbonate.[12] The ester, 0.75 mole, was dissolved in an equal volume of dry ether and added to 2 moles of methylmagnesium chloride. The yield of dimethyl-*tert*-amylcarbinol was 78%. The material from two runs (145 g.) was distilled through column K under reduced pressure to give 135 g. of

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(6) Whitmore and Lux, THIS JOURNAL, 54, 3448 (1932).

(7) Constructed by C. W. Nash of this Laboratory.

(8) Wilson, Parker and Laughlin, THIS JOURNAL, 55, 2795 (1933).

(9) Adams, Adams, Hill and Flosdorf, "Organic Syntheses," Vol. V, 1925, pp. 87, 91.

(10) Whitmore and Church, THIS JOURNAL, 54, 3710 (1932).

(11) Prepared by E. E. Stahly of this Laboratory.

(12) Whitmore and Badertscher, THIS JOURNAL, 55, 1563 (1933).

carbinol, b. p. 86.5° (60 mm.), n^{20}_{D} 1.4420, d^{20}_{4} 0.861. The carbinol was dehydrated by twice distilling from 0.1 g. of β-naphthalene sulfonic acid through a steam-jacketed condenser. After drying with 5 g. of potassium carbonate and 0.5 g. of sodium, the olefin was distilled rapidly through column K and again dried over 0.1 g. of sodium. The yield was 112 g. (96.5%).

Isolation and Identification of the Rearrangement Product.—The olefin mixture (112 g.) was distilled through column N with a reflux ratio of more than 50:1. Fourteen fractions (90 cc.) were collected, b. p. 106.0–107.4° (732 mm.), n^{20}_{D} 1.4178–1.4183. The middle fractions were used to determine the physical properties of 2,3,3-trimethylpentene-1. The residue, 27 cc., was distilled through column K to give six fractions b. p. 107.5–108.7° (743 mm.), n^{20}_{D} 1.4187–1.4198, and a residue of 4.5 cc. This was distilled from a small flask to give a liquid of n^{20}_{D} 1.4260. The six fractions and residue were combined (17 g.) and ozonized as usual,[10] using an ether wash bottle to collect the acetaldehyde. The acetaldehyde-ammonia formed, m. p. 90.5–91°, did not lower the m. p. of a known sample. The oily layer was distilled through column L and the fraction (1 cc.) b. p. 100–110° (732 mm.), n^{20}_{D} 1.3983, was identified as methyl *tert*-butyl ketone by conversion to the 2,4-dinitrophenylhydrazone, m. p. 123–124°, which did not lower the m. p. (125°) of a known sample. The formation of acetaldehyde and methyl *tert*-butyl ketone by ozonolysis proves the presence of 2,2,3-trimethylpentene-3. The refractive index of the original mixture of olefins (1.4182) shows that this olefin was less than 6% of the total.

Preparation of Pentamethylacetone.— (1) *Tert*-butylisopropylcarbinol was prepared in 35% yield from isobutyraldehyde, b. p. 62.3–62.9° (735 mm.), and *tert*-butylmagnesium chloride.[13] The crude carbinol of n^{20}_{D} 1.428 was oxidized with chromic acid at 40° giving a 67% yield of pentamethylacetone,[14] b. p. 133–135° (738 mm.), n^{20}_{D} 1.4057, oxime m. p. 139–140°.[15]

(2) Methyl *tert*-butyl ketone, dimethylated in one operation by the sodamide method,[16] gave a 33% yield of pentamethylacetone. One mole of methyl *tert*-butyl ketone, b. p. 104–106° (739 mm.),[9] was dissolved in 1 liter of dry ether and 200 cc. of dry benzene. One mole (50 g. of 80%) of finely ground sodamide was added and the mixture was refluxed vigorously with good stirring for two hours. The mixture was cooled and one mole of methyl iodide was added over a period of two hours. After refluxing for fifteen minutes, the mixture was cooled, 1.4 moles (70 g.) of sodamide was added and the refluxing was continued until no more ammonia was evolved. The mixture was cooled and 1.75 moles of methyl sulfate dissolved in an equal volume of dry ether was added slowly, then refluxed for half an hour. The excess methyl sulfate was decomposed by vigorously stirring overnight with 200 cc. of water and 100 cc. of ammonium hydroxide. The upper layer was washed with 100 cc. of 5% sulfuric acid, 100 cc. of 5% sodium carbonate, and dried over 25 g. of potassium carbonate. After removal of the ether and benzene the residue was treated with 50 cc. of phenylhydrazine to remove any ethyl *tert*-butyl ketone, and the mixture was distilled to a residue of 50 cc. The distillate was washed with four 100-cc. portions of dilute hydrochloric acid, 100 cc. of water, and dried over 10 g. of potassium carbonate, giving 76 g. of material which was distilled through the 65 × 2.3 cm. column, collecting 42 g. of pentamethylacetone, b. p. 132–134° (730 mm.), n^{20}_{D} 1.4082, yield 33%. On account of the toxicity of methyl sulfate and phenylhydrazine, all the above operations were carried out in a good hood.

(3) Pentamethylacetone was prepared in 54% yield by treating diisopropyl

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(13) Whitmore and Houk, This Journal, 54, 3714 (1932).

(14) Faworsky, *J. prakt. Chem.*, [2] 88, 651 (1913).

(15) Nef, *Ann.*, 310, 329(1900).

(16) Haller and Bauer, *Ann. chim. phys.*, [8] 29, 318 (1913).

ketone[17] in toluene solution with sodamide and methyl sulfate as above. The combined product from three runs was 227 g., b. p. 133–134° (739 mm.), n^{20}_{D} 1.4071.

Preparation and Dehydration of Methylisopropyl-*tert*-butylcarbinol.—Pentamethylacetone, 2.1 moles, with 2.25 moles of methylmagnesium chloride gave a 67% yield of the carbinol, b. p. 62° (12 mm.), n^{20}_{D} 1.4440, d^{20}_4 0.856. A second run gave a 68% yield.

(A) The carbinol, 90 g., was dehydrated with a crystal of iodine under a 90 × 2 cm. column provided with a water separator at its top. The dried olefin mixture (82% yield) was distilled through the Johnston column to give fourteen fractions (total 49 g.) and a residue of 19 g., n^{20}_{D} 1.4302: fractions 1–2, 7 g., n^{20}_{D} 1.4149; fractions 3–14, 42 g., n^{20}_{D} 1.4159–1.4163, Cottrell b. p. 120.1° (734 mm.).

(B) The carbinol, 130 g., was dehydrated by distilling from 0.1 g. of β-naphthalene sulfonic acid through a steam-jacketed condenser, giving a 92.5% yield of dried olefin. This was distilled through the Johnston column to give 27 fractions (total 87 g.) and a residue of 11 g., n^{20}_{D} 1.4357, having a strong odor of the carbinol. Fraction 1, 1.8 g., n^{20}_{D} 1.4152, was not identified. Fractions 2–13, 62 g. 3,3-dimethyl-2-isopropylbutene-1, n^{20}_{D} 1.4174–1.4176, Cottrell b. p. 121.6° (760 mm.), d^{20}_4 0.737, and fractions 23–27, 8 g., 2,3,3,4-tetramethylpentene-1, n^{20}_{D} 1.4305, b. p. 132.6° (743 mm.), d^{20}_4 0.761, were identified by ozonolysis. The intermediate fractions 14–22, n^{20}_{D} 1.4184–1.4298, totaled 14 g. The olefins 3,3-dimethyl-2-isopropylbutene-1 and 2,3,3,4-tetramethylpentene-1 were present in the ratio 3:1 as calculated from the refractive indices.

Identification of 3,3-Dimethyl-2-isopropylbutene-1.—(1) Ozonolysis of fractions 1–14 from (A) 49 g. according to the technique of Church[10] yielded 18 g. of ozonide (33%) which on decomposition gave a strong test[18] for formaldehyde and an oil which was dried and distilled through column B at 739 mm.: fraction 1, 0.5 cc., b. p. 85–123°, n^{20}_{D} 1.3943, fractions 2–4, 7.5 cc., 123–131°, 1.3997, and a residue of 5 cc., 1.4123, were obtained. Fraction 4 was identified as pentamethylacetone by the oxime, m. p. and mixed m. p. 139–140°.

(2) Because of the low yield of ozonide, the process was repeated. The low-boiling olefin (44 g.) from (B) was ozonized and the ozonides were decomposed in the presence of the hydrocarbon solvent.[10] Careful fractionation through Column L showed that only about two-thirds of the olefin had reacted with ozone. The unchanged olefin was again ozonized and again only about two-thirds of it reacted. The ozonolysis products were the same in both cases. The possibility of an equilibrium in ozonization is being further investigated in this Laboratory.

Identification of 2,3,3,4-Tetramethylpentene-1.—Fractions 23–27 from (B) and similar fractions from another preparation (14 g.) were ozonized to give formaldehyde and an oil which was fractionated through Column L to give about 4 cc. of material of b. p. 135–150° (743 mm.), n^{20}_{D} 1.4300, which proved to contain 3,3,4-trimethylpentanone-2. The 2,4-dinitrophenylhydrazone, after five crystallizations from absolute alcohol, melted at 145.5–146.5°. The semicarbazone, crystallized twice from 50% ethanol and once from 50% methanol, melted at 146.5–148.5°. The known semicarbazone kindly supplied by Professor Locquin[19] melted at 147–150° and a mixture melted at 147–149.5°. The structure of the ketone was further proved by oxidation with sodium hypobromite according to the method of Sandborn and Bousquet[20] to give an acid, m. p. 45–47°, and an amide of m. p. 128° which did not lower the melting point of a known sample of dimethylisopropylacetamide prepared from the acid obtained by the action of carbon dioxide on dimethylisopropylcarbinylmagnesium chloride.

Identification of 2,3,4,4-Tetramethylpentene-2.—One fraction from the above

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(17) THIS JOURNAL, 54, 4392 (1932).

(18) Schryver, *J. Chem. Soc.*, Abs., 98, II, 334 (1910).

(19) Locquin and Leers, *Compt. rend.*, 179, 55 (1925); *Bull. soc. chim.*, [4] 39, 436 (1926).

(20) "Organic Syntheses," Vol. VIII, 1928, p. 108.

ozonolysis, 0.5 g., b. p. 95–118° (742 mm.), n^{20}_{D} 1.4090, gave a 2,4-dinitrophenylhydrazone, m. p. 128–129°, which was shown by mixed melting point determinations to be identical with the crystalline modification, m. p. 131°, obtained by melting the known derivative (m. p. 125°) of methyl *tert*-butyl ketone. Thus a small amount of 2,3,4,4-tetramethylpentene-2 occurred in the higher boiling fractions.

Preparation and Dehydration of Methyldi-*tert*-butylcarbinol.—Hexamethylacetone was prepared from diisopropyl ketone by the sodamide synthesis.[16] Three moles, 342 g., of diisopropyl ketone[17] was dissolved in xylene and treated with sodamide and methyl iodide for the first step, sodamide and methyl sulfate for the second. The reaction was carried out without isolating the intermediate product. Because of the difficulty of separating hexamethylacetone from pentamethylacetone and xylene by distillation, the mixture of products was treated with methylmagnesium chloride until a positive test was obtained with Gilman's reagent.[21] The product was worked up as usual and distilled through column A under reduced pressure. The carbinol (135 g.), collected at 122.5–123° (100 mm.), m. p. 42°,[22] represented a yield of 29% from the diisopropyl ketone.

The carbinol, 112 g., was dehydrated by distilling from 0.1 g. of β-naphthalene sulfonic acid through a steam-jacketed reflux condenser. No gas was formed. After drying with 5 g. of potassium carbonate and 1 g. of sodium, the olefin (90 g., 90% yield) was distilled at 731 mm. through the Johnston column to give twenty-five fractions totaling 95.5 cc. and a residue of 11 cc.: fractions 1–2, 3 cc., b. p. 78°, n^{20}_{D} 1.4129–1.4130, rapidly decolorized a solution of bromine in carbon tetrachloride; fractions 3–8, 13.5 cc., n^{20}_{D} 1.4275–1.4362, could not be further separated by redistillation through column L; fractions 9–15, 45 cc., n^{20}_{D} 1.4364, d^{20}_{4} 0.770, Cottrell b. p. 149.5° (760 mm.), were identified as 2-*tert*-butyl-3,3-dimethylbutene-1; fractions 16–25, 34 cc., 1.4365–1.4388, yielded on redistillation through the same column 13 cc. with n^{20}_{D} 1.4364. The residue, 11 cc., n^{20}_{D} 1.4457, distilled from a small distillation flask at 156–185°. The last portion of the distillate solidified in the condenser and was proved by mixed melting point to be unchanged carbinol.

Identification of 2-*Tert*-butyl-3,3-dimethylbutene-1.—A 32-g. portion of fractions 9–15 was ozonized as usual. After fifteen hours the tube plugged due to formation of a solid ozonide. The solution was decanted to another tube and ozonization was completed in less than an hour. The hydrocarbon solution was decomposed as usual, and the solid ozonide was washed into the reaction flask with 300 cc. of acetic acid and likewise decomposed. A positive test for formaldehyde[18] was obtained. The oil layer was dried with 3 g. of potassium carbonate and distilled through column L at 737 mm. to give the principal fractions with b. p. and n^{20}_{D} as follows: 6 cc., 140–149°, 1.4164; 9 cc., 149.0–149.5°, 1.4198; residue, 7 cc., 1.4222. The middle fraction was identified as hexamethylacetone by reaction of 5 cc. with methylmagnesium iodide prepared from 2.4 g. of magnesium and 14 g. of methyl iodide. After decomposing and drying as usual the product distilled from a small distillation flask at 100–117° (100 mm.). The solid carbinol thus obtained, m. p. 41.5°, did not lower the melting point of pure methyldi-*tert*-butylcarbinol. From a consideration of the distillation and ozonolysis results it was concluded that 2-*tert*-butyl-3,3-dimethylbutene-1 constituted over 90% of the dehydration products.

Preparation and Dehydration of Methylethylneopentylcarbinol.—The carbinol was prepared in 67% yield from 2.3 moles of methyl neopentyl ketone, b. p. 123–123.2° (736 mm.), n^{20}_{D} 1.4027, and 2.5 moles ethylmagnesium bromide. The carbinol, 144 g. collected from 62–62.5° (14 mm.), n^{20}_{D} 1.4340, was dehydrated with 3 g. of β-naphthalene sulfonic acid by distilling through a steam-jacketed condenser. The olefin, obtained in 95% yield, was dried over 1 g. of sodium and distilled through the Johnston

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(21) Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925).

(22) Conant and Blatt, *ibid.*, 51, 1236 (1929).

column to give 18 fractions amounting to 120 cc. and a residue of 9 cc., n_D^{20} 1.4292. Cottrell boiling points at 734 mm., n_D^{20} and volumes of the constant refractive index materials were as follows: fractions 5–6, 128.0°, 1.4220, 8 cc.; fractions 12–13, 129.4°, 1.4230, 11 cc.; fractions 17–18, 130.2°, 1.4237, 14 cc.

Identification of the Dehydration Products.—Fractions 2-6, 18 g., gave 20 g. of ozonide which on decomposition gave formaldehyde[18] and 12 g. of an oil layer which was dried and distilled through column B at 725 mm. to give fractions of wts., boiling ranges, and n_D^{20} as follows: No. 1, 2 g., 75–100°, 1.3915; No. 2, 3 g., 100–121°, 1.4035; No. 3, 5 g., 121–126°, 1.4049; No. 4, 1 g., 126–131°, 1.4051; residue, 1 g., 1.4158. Fraction 3 gave a 2,4-dinitrophenylhydrazone m. p. 99° which did not lower the melting point of the derivative prepared from pure methyl neopentyl ketone. From fraction 1, two 2,4-dinitrophenylhydrazones were isolated: one of m. p. 207° which did not lower the melting point of the derivative prepared from known trimethylacetaldehyde, and one m. p. 109–110° which melted at 112° when mixed with the derivative (m. p. 115°) prepared from methyl ethyl ketone. These products proved the presence of 2,2,4-trimethylhexene-4 and 2,2,4-trimethylhexene-3. The presence of 4,4-dimethyl-2-ethylpentene-1 was indicated by the formation of formaldehyde and by the high refractive index of the residue, but attempts to isolate a derivative of ethyl neopentyl ketone were unsuccessful. Since no physical constants for this compound could be found in the literature, it was synthesized from *tert*-butylacetyl chloride and ethylzinc iodide. The following constants for ethyl neopentyl ketone were determined: b. p. 143° (736 mm.), n_D^{20} 1.4110, d_4^{20} 0.812, 2,4-dinitrophenylhydrazone m. p. 135.5°, semicarbazone m. p. 160–161°.

The original olefin fractions 10–14, 23 g., and 15–18, 23 g., gave practically identical results on ozonolysis. The water layers gave no test for formaldehyde,[18] and the oil layers, 15 g. each, gave very similar results when distilled through column B at 727 mm. One of these distillations gave fractions as follows: No. 1, 0.5 g., b. p. 74–100°, n_D^{20} 1.3920; No. 2, 1 g., 100–121°, 1.4014; No. 3, 4 g., 121–123°, 1.4029; No. 4, 3.5 g., 123–124°, 1.4029; No. 5, 1.5 g., 124–126°, 1.4031; No. 6, 1 g., 126–129°, 1.4037; res., 2.5 g., 1.4199. Fraction 3 was identified as methyl neopentyl ketone as before. The distillation and ozonolysis results show that methylethylneopentylcarbinol dehydrates mainly to the ethyl group, with less than 5% dehydrating from the neopentyl group, and only traces due to dehydration from the methyl group. No evidence of rearrangement during the dehydration of methylethylneopentylcarbinol was detected. The expected rearrangement products would yield, on ozonolysis, formaldehyde and 3,4-dimethylhexanone-2, and acetone and methyl *sec*-butyl ketone, respectively. These ketones were not formed. 3,4-Dimethylhexanone-2 has been variously reported with b. p. 152–154°, semicarbazone, m. p. 119°,[23] and b. p. 158°, semicarbazone m. p. 124–126°.[24] The semicarbazone prepared from the residue, n_D^{20} 1.4199, melted at 160–165°, and no material melting lower than 135° could be obtained from the mother liquor, hence no 3,4-dimethylhexanone-2 was present. The other residues proved equally barren of this material.

Methyl *sec*-butyl ketone[25] has b. p. 118°, n_D^{18} 1.4002, semicarbazone m. p. 95.6°. In the search for this material all ozonolysis products were combined and distilled through column L. The semicarbazone prepared from the fraction b. p. 110–120° (736 mm.), n_D^{20} 1.4039, melted at 175° after one crystallization from alcohol (methyl neopentyl ketone semicarbazone m. p. 176°). No material melting lower than 135° could be obtained by fractional crystallization of the mother liquor, so no methyl *sec*-butyl ketone was present. These results prove the absence of rearrangement in the dehydration of methylethylneopentylcarbinol.

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(23) Colonge, *Bull. soc. chim.*, [4] **49**, 444 (1931).

(24) Powell and Secoy, THIS JOURNAL, **53**, 768 (1931).

(25) Beilstein, 4th ed., I, 693 (1918).

Summary

1. The dehydration of tertiary alcohols containing a neopentyl system has been studied with relation to rearrangement.
2. In no case was the rearrangement greater than 25%.
3. No rearrangement took place during the dehydration of methylethylneopentylcarbinol.
4. In the case of methyldi-*tert*-butylcarbinol no rearrangement products were found. Over 90% of the normal dehydration product was isolated.

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The Isoelectric Point of Orange Seed Globulin

BY D. C. CARPENTER AND F. E. LOVELACE

A crystalline protein was first isolated from California orange seed in 1931 by Saunders.[1] He obtained the protein in a crystalline form by dialysis of ammonium sulfate solutions of the protein and named it pomelin. The writers have been unable to obtain a crystalline product from Florida or California orange seed by Saunders' method, the product being in all cases in our experience an amorphous mass instead of definite crystals. However, the writers have been successful in preparing a crystalline globulin from orange seed by an adaptation of the method used by Vickery, Wakeman, and Leavenworth[2] for the extraction of the globulin from tobacco seed and its preparation in crystalline form.

Csonka, Murphy and Jones[3] record the isoelectric point of a number of proteins as deduced from data on minimum solubility. A large amount of their data deals with various plant globulins for which the various individual isoelectric points range between *P*H's 5.0 and 5.5.

The point of electrical neutrality of a colloid may be determined in either of two ways, *i. e.*, by the moving boundary method described by Tiselius[4] in which the movement of a column of colloidal particles under a known potential is measured, or the somewhat different method[5] in which the rate of movement of the individual colloidal particle or an aggregate is observed under the microscope. In many cases a substance such as powdered quartz has been added to a sol on which the colloid was supposedly adsorbed and which powder then behaved as the colloid itself.[6]

From the Helmholtz–Lamb equation $V = \zeta HD/4\pi h$, where V is velocity

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(1) Saunders, THIS JOURNAL, **53**, 696 (1931).

(2) Vickery, Wakeman and Leavenworth, *Conn. Agr. Expt. Sta. Bull.*, [II] **339**, 625 (1932).

(3) Csonka, Murphy and Jones, THIS JOURNAL, **48**, 763 (1926).

(4) Tiselius, *Nova Acta Reg. Soc. Sci. Upsaliensis*, Series IV, **7**, No. 4 (1930).

(5) Northrup, *J. Gen. Physiol.*, **4**, 629 (1922).

(6) Freundlich and Abramson, *Z. physik. Chem.*, **133**, 51 (1928).

of particle, ζ is electrokinetic potential, H is potential gradient per cm., D is dielectric constant of the dispersion medium, and h is viscosity of the medium. In the present paper the values for D and h have been assumed to be those for water, namely, 81 and 0.009, respectively, at 25°. All quantities in the above equation are expressed in c. g. s. electrostatic units.

Preparation of Material.—Whole seeds of the California orange were coarsely ground in a Wiley mill and extracted repeatedly with cold benzene to remove oil, then air dried and ground to pass a one-millimeter sieve. The protein was extracted from the fat-free meal by warm (55°) molar sodium chloride solution in the proportion of one liter of solvent per 100 g. of meal. The mixture was stirred occasionally and, after two hours standing, the liquid was removed from the undissolved matter in a centrifuge. The somewhat turbid centrifugate was filtered through an asbestos and paper pulp filter, after which treatment it was sparkling clear and amber in color. The filtrate was diluted with five volumes of water at 55° and again filtered through asbestos and paper pulp. Toluene was then added as a preservative and the filtrate allowed to stand twenty-four to forty-eight hours at 0°. The protein crystallized out under this procedure in microscopic octahedral crystals which were separated from the mother liquor by centrifuging.

The crystalline protein was redissolved in the least quantity of warm molar sodium chloride solution required, filtered as mentioned before, and again precipitated by dilution, this time adding ten volumes of water at 55° instead of five volumes to effect crystallization. The diluted mixture was allowed to stand overnight at 0° for crystallization of the protein. The crystalline precipitate was separated in a centrifuge, suspended in distilled water and electrodialyzed between parchment membranes to remove the last traces of sodium chloride. After the first crystallization, solutions of the protein in salt solution were colorless. Whether the writers' crystalline preparation is a single chemical entity or not and whether it is the same protein obtained from orange seed by Saunders cannot be judged at present. In Fig. 1 is shown a photomicrograph of one of our preparations.

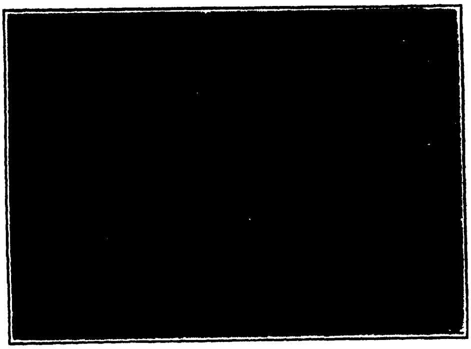

Fig. 1.—Crystalline globulin of orange seed (× 480).

A portion of the crystalline protein was removed before electrodialysis and washed with successive portions of ethyl alcohol of increasing concentrations, finally with ether and then dried in a desiccator. No change in structure could be observed in the crystals under this treatment. For the electrophoretic work to be described, however, electrodialyzed material which had not been alcohol treated or dried was used.

Electrophoresis Experiments.—The solutions of protein were prepared by dissolving about one gram of protein in 100 cc. of each of a series of buffer solutions ($M/30$ after Sörensen) containing the required amount of the proper citrate or phosphate, respectively, to give the desired P_H value over the range P_H 1.5 to 7.8. The actual P_H of each protein solution was determined potentiometrically with the quinhydrone electrode. After preparation the protein solutions were stored a few days at 0° with toluene until the electrophoresis measurements could be completed.

TABLE I

ELECTROPHORETIC VELOCITY AND CALCULATED ζ-POTENTIAL OF ORANGE SEED GLOBULIN

*P*H	Velocity μ/sec./v/cm.	Calcd. ζ-potential, millivolts	*P*H	Velocity μ/sec./v/cm.	Calcd. ζ-potential, millivolts
1.47	+8.2	+103.0	5.43	−2.2	−27.6
1.67	+7.6	+ 95.5	5.57	−2.2	−27.6
1.69	+8.0	+100.5	5.72	−3.7	−46.5
1.71	+7.8	+ 98.0	5.87	−4.8	−60.3
2.00	+7.8	+ 98.0	5.89	−4.9	−61.6
2.43	+7.3	+ 91.7	5.90	−5.2	−65.3
2.84	+6.3	+ 79.2	6.18	−5.1	−64.1
3.36	+6.1	+ 77.6	6.73	−5.4	−67.9
4.53	+5.2	+ 65.3	7.61	−5.7	−71.6
5.02	+1.8	+ 22.6	7.70	−6.3	−79.2
5.32	−0.7	− 8.8	7.76	−6.7	−84.2

The cell used for the electrophoresis work has been described by Northrup.[8] Velocity observations were always made at the same place in the cell, using a micrometer eyepiece. All measurements recorded for a given *P*H are the mean of ten or twelve closely agreeing observations in which the current direction was repeatedly reversed.

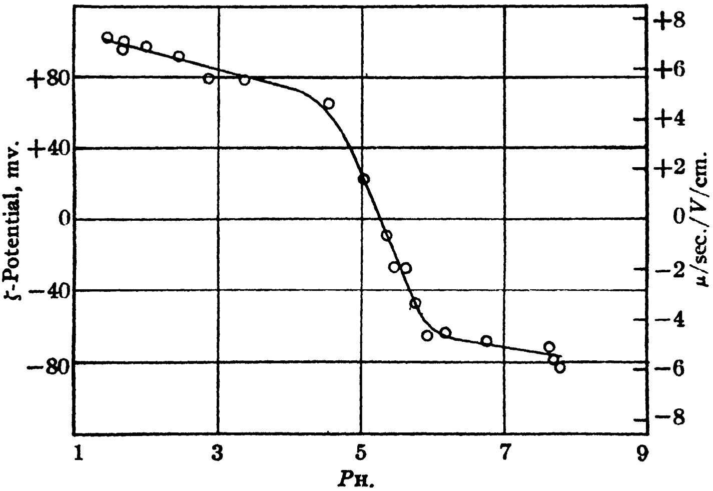

Fig. 2.—ζ-Potential and migration velocity of orange seed globulin.

The data are given in Table I and are presented graphically in Fig. 2. Interpolated from the graph, the isoelectric point of the protein is at *P*H 5.23 or C_H 5.9 × 10^{-6}.

Summary

1. The electrophoretic velocity of orange seed globulin has been measured in citrate and phosphate buffer solutions in the *P*H range 1.5 to 7.8 and the electrical charge on the particle calculated.

2. The isoelectric point of orange seed globulin was found to be at *P*H 5.23 or C_H 5.9 × 10^{-6}.

GENEVA, N. Y.

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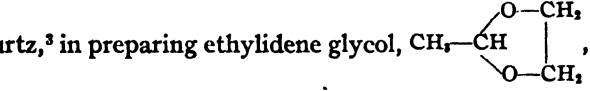
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Formation of Cyclic Acetals from Aldehydes or Ketones and Alkylene Oxides

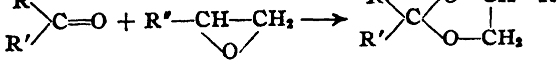
BY MARSTON TAYLOR BOGERT AND RICHARD O. ROBLIN, JR.[1]

Introduction

Cyclic acetals have been the subject of numerous investigations,[2] and in every case their formation has involved the use of a polyhydroxy compound. Wurtz,[3] in preparing ethylidene glycol,  , attempted a direct condensation of ethylene oxide and acetaldehyde, but reported only negative results. Later, Lochert[4] confirmed this observation of Wurtz. He was unable to obtain a reaction between propylene oxide and acetaldehyde. More recently[5] negative results have also been reported in the case of benzyl ethylene oxide, when 40% sulfuric acid was used as a catalyst.

When dioxane is prepared from ethylene oxide in the presence of a catalyst, some cyclic acetal is formed.[6] It has been suggested that the acetal formation involved a rearrangement of ethylene oxide to acetaldehyde, which then reacted with more ethylene oxide to form ethylidene glycol. While up to the present time there has been no direct experimental basis for the second step in this hypothesis, it has been generally accepted, and has even crept into textbooks as a reaction of ethylene oxide.[7]

During a study of the properties of ethylene oxides in this Laboratory, it was discovered that these compounds react with aldehydes and ketones in the presence of metallic chlorides. The resulting compounds are cyclic acetals, the formation of which may be typified as follows



In so far as we have been able to determine, this is the first time that the reaction of ethylene oxides with aldehydes or ketones has been carried out successfully.

Since the reaction does not take place in the absence of a catalyst, any hypothetical mechanism must take cognizance of this fact. It is well established that stannic chloride forms addition compounds with ethers and carbonyl compounds.[8] The addition of stannic chloride to benzaldehyde, for example, causes the precipitation of a solid complex, which gradually dissolves as ethylene oxide is introduced. This may be due to the formation of a soluble addition compound between ethylene oxide and stannic chloride, which, in turn, interacts either with free benzaldehyde, or the benzaldehyde–stannic chloride complex, I, as follows

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[1] This research could not have been carried out but for the generous assistance of Mr. G. A. Pfeiffer, President, Richard Hudnut, New York, N. Y., the donor of the fellowship held by the junior author; and of Dr. George O. Curme, Jr., Vice President, Carbide & Carbon Chemicals Corporation, New York, N. Y., who very kindly supplied the requisite alkylene oxides.—M. T. B. and R. O. R., Jr.

[2] (a) Fischer, *Ber.*, **27**, 1524 (1894); (b) **28**, 1979 (1895); (c) Fischer and Pfähler, *ibid.*, **53**, 1606 (1920); (d) Irvine, *J. Chem. Soc.*, **103**, 575 (1913); (e) **107**, 337 (1915); (f) Hibbert and co-workers, THIS JOURNAL, **45**, 734; (g) 3108 (1923), *et seq.*; (h) *Can. J. Research*, **2**, 35; (i) 131; (j) 214 (1930).

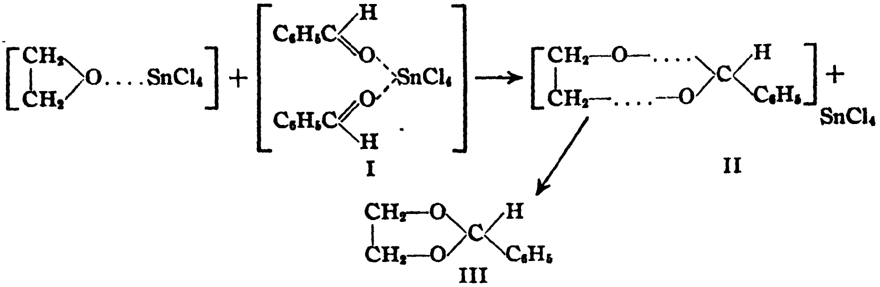
[3] Wurtz, *Ann.*, **120**, 328 (1861).

[4] Lochert, *Ann. chim. phys.*, [6], **16**, 56 (1889).

[5] Read, Lathrop and Chandler, THIS JOURNAL, **49**, 3116 (1927).

[6] Faworski, *J. Russ. Phys.-Chem. Soc.*, **38**, 741 (1906); *Chem. Zentr.*, **78**, I, 15 (1907).

[7] Richter–Anschütz, "Chemie der Kohlenstoffverbindungen," 1928, 12th ed., Vol. I, pp. 402–403.



As will be seen in II, this involves the simultaneous opening of the three membered oxide ring and the two membered carbonyl ring. If these two unstable systems combine, the cyclic acetal III will be formed. The benzaldehyde is written in the form of its stannic chloride complex rather than in the free form, because this solid complex does not disappear until the reaction is practically complete.

The course of the reaction, in the case of benzaldehyde, may be followed by observing the color changes which take place. As ethylene oxide is added the liquid becomes red in color. The red color gradually deepens until, near the end of the reaction, a green fluorescence appears. When the reaction is complete the solution is a clear green. If this green solution is allowed to stand in the presence of sunlight, it fades to a pale yellow, but it persists indefinitely in the absence of light. The red color was shown to be due to the benzaldehyde–stannic chloride complex in solution, while the green color could be produced by the addition of stannic chloride to the pure cyclic acetal. The low yield may be accounted for, in part, by this cyclic acetal complex, which removes stannic chloride from the reaction. When acetophenone or methyl hexyl ketone is used, the solution becomes orange, and this color persists during the reaction. Here, too, the color is sensitive to sunlight. No color appears when heptaldehyde is used.

Experimental

Since a trace of water is detrimental to the reaction, the starting materials were thoroughly dried. In the case of ethylene oxide this was accomplished by passing the gas over soda lime, as recommended in "Organic Syntheses."[9] The propylene oxide and other starting materials were purified by two fractional distillations.

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(8) Pfeiffer, *Ann.*, **376**, 285 (1910); (b) **412**, 253 (1916); (c) *Ber.*, **44**, 2653 (1911); (d) *Z. anorg. Chem.*, **87**, 335 (1914); (e) Weinland, "Komplex-Verbindungen," Stuttgart, 1919, p. 236.

(9) "Organic Syntheses," John Wiley and Sons, New York, 1926, Vol. VI, p. 54.

Preparation of Cyclic Acetals

After a number of experiments, the following conditions were selected as giving the best results: 0.2 mole of the aldehyde or ketone was cooled in an ice-bath to 5°, and 0.01 mole of anhydrous stannic chloride added slowly from a graduated pipet. A complex formed which in the case of benzaldehyde and acetophenone was a white solid; 0.25 mole of the oxide was then added gradually with occasional shaking. The temperature was maintained between 40–50° throughout the addition, which generally required about eighty minutes. The clear solution[10] was allowed to cool to room temperature, and an equal volume of benzene added, the mixture washed with three 10-cc. portions of 10% sodium hydroxide to remove the stannic chloride, and then with three 10-cc. portions of water. The resulting benzene solution was dried over anhydrous sodium sulfate, the benzene removed on a steam-bath, and the product fractionated; yield, 25-35%.

Attempts to increase the yields were unsuccessful because of two opposing factors. The amount of cyclic acetal formed was shown to be directly proportional to the amount of stannic chloride used, and also to the temperature of the reaction. However, these factors bore a similar relation to the formation of a high boiling material, probably a polymer. Thus, the use of larger relative amounts of stannic chloride resulted in the recovery of less of the original carbonyl compound, but a larger amount of the "polymer" was formed; so that the yield of cyclic acetal had not been increased and may even have been decreased. The same was true of the temperature; high temperatures favored the reaction, but also favored "polymerization." The procedure described above represents the optimum conditions possible in the face of these opposing factors. The use of solvents such as ether, benzene or carbon tetrachloride did not give an appreciable increase in the yield. Benzene was found to be the best solvent, while ether actually inhibited the reaction.

Under the same experimental conditions the following catalysts produced only a trace of the desired product: $SnCl_4 \cdot 4H_2O$, $ZnCl_2$, $FeCl_3$, $SbCl_3$, $AlCl_3$.[11] $CaCl_2$, NH_4Cl, HCl, H_2SO_4 and $POCl_3$ gave no appreciable reaction.

Formation of the "Polymer" and Reversibility of the Reaction.—The formation of the high boiling material seriously decreased the yield, and an attempt was made to determine its constitution. If the residue consists of polymerized acetal it should be possible to obtain a quantitative hydrolysis to the original aldehyde or ketone and the corresponding glycol. The residue resulting from the reaction of benzaldehyde and ethylene oxide was, therefore, heated at 150° and 20 mm. for three hours to remove as much of the lower boiling material as possible. Ten grams of the resulting residue was refluxed with dilute hydrochloric acid for one-half hour. This treatment resulted in the formation of only a trace of benzaldehyde. The remainder of the material was recovered unchanged. Since, under the same conditions, benzylidene glycol is hydrolyzed quantitatively to benzaldehyde and ethylene glycol, it would appear that the high boiling residue is not a polymer of the cyclic acetal. An attempt to distil the high boiling "polymer" at 20 mm. pressure produced a slow decomposition. Benzaldehyde was the only definite compound which could be isolated from the resulting distillate.

The reaction was shown to be non-reversible by the following experiment: 10 g. of pure benzylidene glycol was heated in a distilling flask with 0.7 g. of anhydrous stannic chloride at 50° for one hour. The receiver was immersed in solid carbon dioxide, but no ethylene oxide was liberated, and the original material was recovered unchanged.

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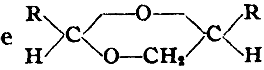
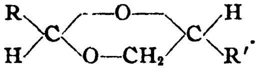
(10) In the case of acetophenone and ethylene oxide, the ketal separated as a crystalline solid. By cooling to −5° practically all of the material separated from the reaction mixture. It was dissolved in ether, washed and dried in the usual manner, and purified by fractional distillation *in vacuo*.

(11) Because of the tendency of this salt to resinify the carbonyl compound only 0.003 mole could be used.

The following cyclic acetals and ketals were prepared by the procedure described above.

Compound (1,3-dioxolane)	B. p., (corr.), °C.	Yield, %	Analyses Calcd. C	Analyses Calcd. H	Analyses Found C	Analyses Found H
2-Phenyl-[12a] (benzylidene glycol)	225	35	..	..	..	..
4-Methyl-2-phenyl-	118 (23 mm.)	30	73.1	7.3	72.9	7.5
2-Hexyl-[12b,13]	200	25	..	..	..	..
4-Methyl-2-hexyl-	102.5–103.5 (23 mm.)	22	69.7	11.6	69.6	11.7
2-Methyl-2-hexyl-	97 (23 mm.)	25	69.7	11.6	68.9	11.9
2,4-Dimethyl-2-hexyl-	102 (23 mm.)	30	70.9	12.0	70.5	12.2
2-Methyl-2-phenyl-[14]	103.5–104.5 (23 mm.)	28	73.1	7.3	73.1	7.3
2,4-Dimethyl-2-phenyl-	105 (23 mm.)	32	74.1	7.9	73.8	7.9

2-Phenyl-1,3-dioxolane and 2-hexyl-1,3-dioxolane were identified by their boiling points, and by comparison with the same compounds prepared from ethylene glycol. In every case the compounds were readily hydrolyzed by dilute acid to the corresponding aldehyde or ketone.

Hibbert[15] has shown that compounds of the type  are capable of existing in two isomeric forms. These isomers are accounted for by the different relative positions of the groups R and R′, and may be considered as *cis* and *trans* isomers. In this case the *trans* form would be represented by the formula . All of the compounds in this paper, which were prepared from propylene oxide, should show this type of isomerism, in addition to optical isomerism. Since none of these compounds were solids, no method could be devised for separating the isomers.

While the preparation of cyclic acetals from ethylene or substituted ethylene glycols is quite satisfactory in most cases, the cyclic ketals are prepared only with difficulty and in very small yields.[16] Thus, by the use of ethylene glycol in the presence of 40% sulfuric acid, the authors were unable to prepare even a trace of the cyclic ketal of acetophenone.[17] Although the method described in this paper is not entirely satisfactory, it furnishes a simple approach to cyclic ketals which are difficult or impossible to make by the usual method.

The polysubstituted ethylene oxides in which more than one hydrogen is replaced have not been studied. However, it may be anticipated that these compounds will react in an analogous manner, at least in the case of

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(12) (a) Hibbert and Timm, THIS JOURNAL, 46, 1283 (1924); (b) Dworzak and Herrmann, *Monatsh.*, 52, 83 (1929).

(13) Lochert, *Ann. chim. phys.*, [6] 16, 26 (1889).

(14) Crystallized from ether in large flat plates, m. p. 62° (corr.), soluble in alcohol, toluene, carbon tetrachloride, petroleum ether, acetone and glacial acetic acid; insoluble in water.

(15) Hibbert and Carter, THIS JOURNAL, 50, 3376 (1928).

(16) (a) Böeseken and Hermans, *Rec. trav. chim.*, 42, 1104 (1923); (b) Dworzak and Herrmann, *Monatsh.*, 52, 83–106 (1929).

(17) *Cf.* Fröschl and Heuberger, *Monatsh*, 59, 289 (1932).

the simpler derivatives. An investigation of the higher membered oxides such as trimethylene oxide and tetrahydrofuran was not undertaken, since the lesser reactivity of these compounds made it seem doubtful that an appreciable reaction would take place.

Summary

Ethylene oxides react with aldehydes and ketones in the presence of metallic chlorides to form cyclic acetals, in yields varying from 25 to 35%.

By this method six new acetals and ketals were prepared, some of which would be difficult or impossible to make by the use of a glycol.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of Oxidation-Reduction Potentials in Glacial Acetic Acid Solutions

BY J. B. CONANT AND B. F. CHOW

It was shown eight years ago[1] that the ion of a halochromic salt and a free radical such as triphenylmethyl form a mobile oxidation-reduction system whose potential can be measured in a non-aqueous medium. The lack of adequate information about the properties of acids and bases in such non-aqueous media prevented a detailed quantitative study of the problem at that time. A study of glacial acetic acid solutions was undertaken therefore, and has now reached a point where it is possible to return to the study of oxidation-reduction potentials in this and similar non-aqueous media. In this paper we shall present the results of the study of certain dyes and quinones of the type which has been studied extensively in water; in a later paper we shall consider the rather unique system composed of a free radical and a halochromic salt.

The measurements were all made using glacial acetic acid as the solvent. The hydrogen-ion activity was kept constant in each experiment by means of suitable "buffers," which in most instances consisted of an organic base partially neutralized with sulfuric acid. The ionic strength was constant at 0.2 in all the buffers, and where necessary a neutral salt was added to bring the value of the ionic strength to 0.2. The exact composition of the buffers is given in Table I together with the $(P\text{H})^{\text{HAc}}$ values determined by means of a chloranil electrode as previously described in papers from this Laboratory.

The Acidity Scale in Acetic Acid

A few words are necessary in regard to the significance of the $(P\text{H})^{\text{HAc}}$ values. Since the first work from this Laboratory on glacial acetic acid,

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[1] Conant, Small and Taylor, THIS JOURNAL, 47, 1959 (1925).

TABLE I

COMPOSITION OF BUFFERED GLACIAL ACETIC ACID SOLUTIONS

The glacial acetic acid employed melted at 16.5°. Solution 10 was not very stable. In two weeks time its P_H changed from −0.95 to +0.02. Only the freshly made solutions were used in the experiments. Unless otherwise noted the neutral salt added was trimethylammonium *p*-toluene sulfonate.

Soln.	Concn. of base in moles per liter	Neutralized with H_2SO_4, %	Moles of neutral salts per liter	$(P_H)^{HAc}$	
1	1.0 Pyridine	0	0.200	+4.24	
2	0.1 Pyridine	0	.200	+3.64	+3.52
3	.05 Acetoxime	0	.200	+2.47	+2.29
4	.05 Antipyrine	50	.175	+1.66	
5	.05 Urea	0	.200	+1.86	+1.61
6	.05 Acetoxime	50	.175	+1.00	
7	.05 Urea	15	.1925[a]	+0.34	
8	.30 Acetoxime	65	.005	+ .25	
9	.25 Acetoxime	80	.000	− .15	
10	.05 Acetamide	70	.163	− .98	
11	.1 Benzamide	9	.110	−2.10	

[a] Indicates that the neutral salt was triethylammonium perchlorate. A partially neutralized urea buffer of $(P_H)^{HAc}$ value −0.63 with somewhat less ionic strength was also used in some experiments.

it has become evident that it is impossible to relate the fugacities of an individual ion from two solvents. It has further become evident[2] from a series of experimental results in acetic acid solutions of varying ionic strength that the relation of the base strength of two bases in acetic acid and in water depends on (a) the charge of the base, and (b) the ionic strength of the acetic acid. For practical purposes a very dilute solution of a base in acetic acid is of no value, but a solution containing enough neutral salt so that $\mu = 0.2$ is conveniently prepared. Slight changes in ionic strength at this point have little effect, although a change of the neutral salt may cause shifts in the apparent $(pK)^{HAc}$ value of as much as 0.5 of a unit (see Fig. 3, Conant and Werner, THIS JOURNAL, 52, 4442 (1930)).

Hammett and Deyrup[3] have greatly clarified the subject of non-aqueous solutions by defining an acidity function of such solutions by the equation

$$H_0 = -\log a_{H^+}(f_B/f_{BH^+})$$

The acidity function will depend on the charge on the base and they propose the symbol H_0 for bases like urea, H_- for bases like the acetate ion, etc. To the extent that the ratio f_B/f_{BH^+} in a given solution is the same for all bases, this definition is exact and has real meaning. The pK'_B value of a base defined in terms of this scale of acidity function is independent of the solvent to the extent that the assumption just mentioned is exact. We may now redefine our $(P_H)^{HAc}$ scale in terms of Hammett and Deyrup's

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(2) Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929).

(3) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

acidity function referred to a base of the zero charge type (H_0) and defining our solvent as glacial acetic acid with neutral salt added to give $\mu = 0.2$.

The best comparison now available of the relative strengths of two bases in water and an acetic acid solution of high ionic strength is given in Fig. 4, of the paper by Conant and Werner. From the data there given the apparent pK values of urea and acetoxime are $+1.1$ and $+0.3$, the corresponding values in water are about $+1.75$ and $+0.1$; the uncertainties in the acetic acid values are at least ± 0.2 and the values in aqueous solution of such very weak bases may be in error to a considerable extent. The zero point of the $(P\text{H})^{\text{HAc}}$ scale was originally chosen in part because the value of $(pK)^{\text{HAc}}$ for urea titrated in a 0.2 M solution ($\mu = 0.2$ at the midpoint) closely coincided with the pK value in water. It is evident that if urea is used for the comparison, $(P\text{H})^{\text{HAc}} = H_0$ within the limits of experimental error; if acetoxime is used for the comparison, the old $(P\text{H})^{\text{HAc}}$ scale should be corrected by about 0.6 of a unit. The discrepancy between these two bases of the same charge type may in part reflect experimental uncertainties but may also represent the limit of accuracy of the assumption that $f_{\text{B}}/f_{\text{BH}^+}$ for the two bases is the same. At all events, it seems best to continue the use of the old $(P\text{H})^{\text{HAc}}$ scale for acetic acid solutions where $\mu = 0.2$, as any correction of it to make it coincide more closely with the H_0 scale is perhaps impossible.

It should be borne in mind that at low values of μ, the $(P\text{H})^{\text{HAc}}$ scale must be corrected to make it correspond even approximately with the H_0 scale. For example, at $\mu = 0.025$ (the half-neutralized base contributing the salt), Hall[4] found a fairly consistent spread of about 2 units between $(pK)^{\text{HAc}}$ (defined on the old $(P\text{H})^{\text{HAc}}$ scale) and $pK^{(\text{H}_2\text{O})}$ for a variety of bases of the zero type. Therefore at $\mu = 0.025$, $H_0 \cong (P\text{H})^{\text{HAc}} + 2$. The irregularities may be certainly as much as 0.5 of a unit, however. The impossibility of making any of these definitions exact must be emphasized; the assumption of the constant ratio of the activity coefficients is certainly inexact and in solutions of high ionic strength experiment has shown that the nature of the neutral salt may affect the apparent pK values by several tenths of a unit.

The Measurement of Oxidation–Reduction Potentials

We shall define our oxidation–reduction potentials (E_{h}) in glacial acetic acid solutions with reference to a hypothetical hydrogen electrode (1 atm.) functioning in a buffered solution of ionic strength 0.2 and $(P\text{H})^{\text{HAc}} = 0$. Actually the oxidation–reduction half-cell was measured against a saturated aqueous calomel electrode through a lithium chloride bridge. Since the same arrangement was used in measuring the $(P\text{H})^{\text{HAc}}$ values of the buffer with the chloranil electrode, the aqueous electrode and the salt bridge cancel in the final calculations. By the definition of our original

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(4) Hall, This Journal, 52, 5115 (Fig. 2) (1930).

$(P\text{H})^{\text{HAc}}$ scale, the saturated chloranil electrode at $(P\text{H})^{\text{HAc}} = 0$ was given the value of +0.566 referred to aqueous calomel through the lithium chloride bridge.[1a] The value of the saturated chloranil electrode against the hydrogen electrode is independent of the solvent and has the value +0.664. From this it follows that the potential of a hypothetical hydrogen electrode in acetic acid $(P\text{H})^{\text{HAc}} = 0$, against aqueous calomel is $0.566 - 0.664 = -0.098$ volt (European convention in regard to sign). The value of E_h of the oxidation–reduction potential is thus 98 millivolts greater than the observed potentials measured against the aqueous calomel electrode.

The apparatus used was very similar to that employed in the measurement of $(P\text{H})^{\text{HAc}}$ values (see Fig. 6, Ref. 1). The stirrer was omitted and an inlet tube for oxygen-free nitrogen dipped well beneath the liquid. The air-tight rubber stopper carried two bright platinum electrodes, a buret tip and an exit tube. A slow stream of nitrogen supplied sufficient agitation. The temperature was 25 ± 2°. Two methods of varying the ratio of oxidant and reductant were employed. One was the well-known method of mixtures, the other was by titration of the oxidant with chromous acetate. The reductant in most cases was prepared by reducing the oxidant with hydrogen and platinized asbestos; the solution was kept in a reservoir connected to a buret in an atmosphere of oxygen-free nitrogen. Five cc. of buffer solution was placed in the cell in each experiment and 0.25 to 1.00 cc. of a 0.0060 *M* solution of the oxidant or reductant added; the total concentration of oxidant and reductant at the midpoint was therefore about 0.0017 molar.

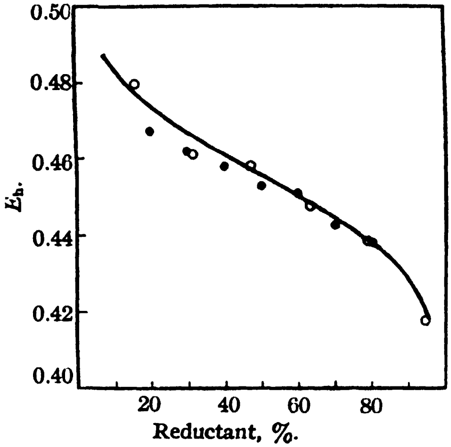


Fig. 1.—Showing the relation between the potential and the varying ratios of oxidized and reduced *o*-cresol-indophenol in $P\text{H}$ +2.32: ●, method of mixtures; ○, method of titration. The curves were drawn with the theoretical slope through the average $E_h^{0\prime}$.

The accuracy of the results is, of course, much less than that obtained using aqueous solutions. Figures 1 and 2 illustrate typical results. In Fig. 1 are plotted results obtained by the method of mixtures and by titration (using $Cr(Ac)_2$); the usual sigmoid curve was drawn to correspond to the equation

$$E_h = E_h^0 + \frac{RT}{2F}\ln\frac{[\text{Oxid.}]}{[\text{Red.}]}$$

The value of E_h^0 obtained by considering the titration results alone was 0.455 and that obtained from the method of mixtures 0.453. In Fig. 2 a logarithmic plot presents the results obtained with indothymol in four different buffers by the method of mixtures. The straight lines are drawn with a slope corresponding to the equation given above. The value of E_h^0 calculated from all the points in an experiment usually deviated not more than ±2 millivolts from the average value. In the case of benzoquinone at $(PH)^{HAc} = +3.52$, both the titration method and the method of mixtures gave a value of E_h^0 identical within half a millivolt.

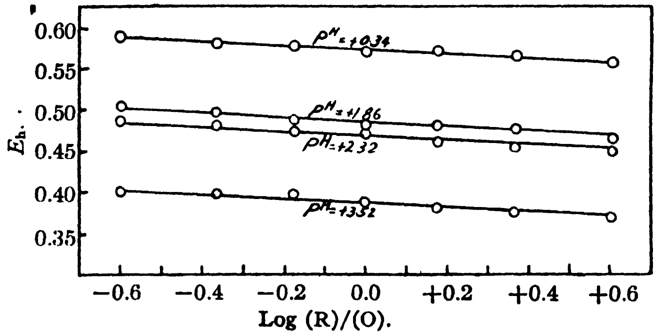


Fig. 2.—Potentials of indothymol in different PH. Lines are drawn with the theoretical slope.

The values of E_h^0 are plotted against $(\text{PH})^{HAc}$ for five compounds in Fig. 3. The values for chloranil and benzoquinone were obtained simply

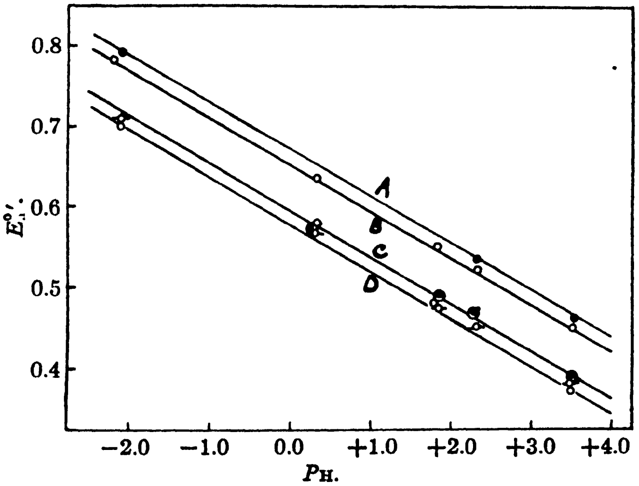
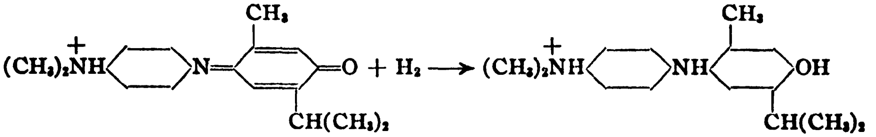


Fig. 3.—Showing the relationship between PH and $E_h^{0\prime}$. The lines were drawn with the theoretical slope: A, chloranil; B, benzoquinone; C (●), indothymol; D, -O- indo-o-cresol; ○ o-cresol-indophenol.

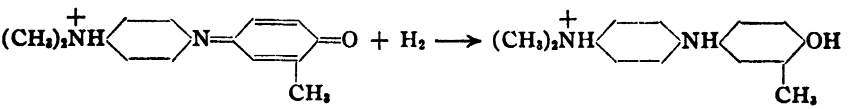
by using an equimolecular mixture of the reductant and oxidant in each buffer (except $(\text{PH})^{HAc} = 3.52$ where the titration method was also employed with benzoquinone). The values for the three dyes are the average of a number of points obtained by the method of mixtures or in a few cases by titration with chromous acetate as explained above. To save space we are omitting the several hundred individual determinations of E_h from which the average values of E_h^0 were calculated for each buffer. The slope of the lines in Fig. 3 corresponds to $\Delta E_h^0/\Delta(P_H) = -0.060$. A close agreement of the experimental points to this line is, of course, to be expected in the case of quinone and tetrachloroquinone (chloranil) since the dissociation of the phenolic groups lies far beyond the most alkaline end of this range of $(P_H)^{HAc}$ values (much more alkaline than can be reached in glacial acetic acid, in fact). The value of E_h^0 at $(P_H)^{HAc} = 0$ corresponds to the free energy of the reduction of the quinone by hydrogen; we shall designate it as E'_0. The values from Fig. 3 are 0.675 for chloranil and 0.650 for benzoquinone. These values differ from those in alcoholic solution which are 0.703 and 0.711, respectively, as might be expected. The fact that chloranil in acetic acid is a stronger oxidizing agent than benzoquinone is of interest as the free energies referred to the gaseous state are in the same order with even a greater difference between the two compounds.[5]

The equations for the reduction of the three dyestuffs in the range of acidity we are here concerned with, are as follows

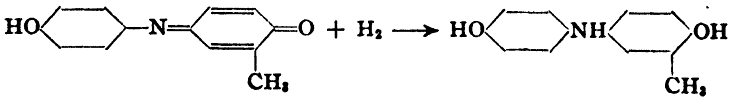
(1) Indothymol: $E_0^1 = 0.600$



(2) Indo-o-cresol: $E_0^1 = 0.575$



(3) o-Cresol-indophenol: $E_0^1 = 0.575$



The free energy of each of the reactions written above is equal to $-2FE'_0$ where E'_0 is the value of E_h^0 at $(P_H)^{HAc} = 0$. The values of E'_0 given above were obtained by graphical interpolation of the lines of Fig. 3. Any differences between E'_0 for (2) and (3) are within our experimental error, which is probably as much as ±7 millivolts because of the difficulties attending the preparation and measurement of $(P_H)^{HAc}$ of the buffer solutions. The small difference between even (1) and (3) is not surprising

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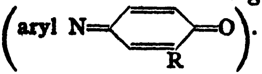
(5) This Journal, 49, 293 (1927).

since in all three cases the group undergoing reduction is very nearly the same  The linear relationship between $(P\text{H})^{\text{HAc}}$ values and E^0_{h} is surprising since it might be expected that the diphenylamine grouping of the reductant would unite with a proton at about $(P\text{H})^{\text{HAc}} = 0$. (The value of pK_{B} for diphenylamine is about 0.) This should result in a bend of the curve as many examples studied in aqueous solution have shown. Evidently the hydroxyl group in the para position has made the base still weaker than diphenylamine.

In all the experiments recorded in this paper, the ionic strength of the glacial acetic acid solutions has been kept constant at $\mu = 0.2$. In such a solvent $(P\text{H})^{\text{HAc}} = H_0$ as explained early in this paper. H_0, therefore, might replace $(P\text{H})^{\text{HAc}}$ in the plot in Fig. 3 without change It is interesting to note that if the oxidation–reduction potential of one of the substances is determined in a buffer solution of different ionic strength, the result will also fall on the straight line of Fig. 3, but the position of the point will then depend on whether $(P\text{H})^{\text{HAc}}$ (as defined in all our work) or H_0 is plotted horizontally.

Summary

It has been shown that the oxidation–reduction potential of quinones and certain dyes may be measured in glacial acetic acid by the method of mixtures or by titration of the oxidant with chromous acetate. The results obtained in a series of buffers with constant ionic strength lie on a straight line with the theoretical slope when E^0_{h} is plotted against $(P\text{H})^{\text{HAc}}$. The relation of the $(P\text{H})^{\text{HAc}}$ scale to Hammett and Deyrup's acidity function is discussed briefly.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Potential of Free Radicals of the Triphenylmethyl Type in Glacial Acetic Acid Solutions

BY J. B. CONANT AND B. F. CHOW

In a preceding paper[1] it was shown that the oxidation-reduction potentials of quinones and certain dyes could be measured in a series of glacial acetic acid buffer solutions by the usual procedure. In this paper we shall consider the application of these methods to the problem of the potential between a free carbon radical and a halochromic salt—a problem stated and partially solved in an earlier paper from this Laboratory.[2] The buffer solutions employed were the same as those used in the preceding paper and their $(P\text{H})^{\text{HAc}}$ values were measured with the chloranil electrode as previously described.

The electrode reaction involved in all the cases studied may be written in the general form

$$\underset{\text{(halochromic ion)}}{R_3C^+} + e \rightleftharpoons \underset{\text{(free radical)}}{R_3C}$$

At constant hydrogen-ion activity the potential will depend on the relative amounts of the halochromic ion and free radical according to the usual electrochemical equation (1).

$$E_h = E_0 + \frac{RT}{F}\ln\frac{[R_3C^+]}{[R_3C]}$$

As usual, the potential is referred to a hypothetical hydrogen electrode operating in a buffer solution in glacial acetic acid of $(P\text{H})^{\text{HAc}} = 0$. The relation of this scale to Hammett and Deyrup's acidity function has been discussed in the preceding paper.[1] The relation between the concentration of free radical and the total reductant expressed as moles of ethane (associated form) is as follows $[R_3C] = 2\alpha[\text{Ethane}]_T$. At a given dilution and temperature we may consider that α, the degree of dissociation of the ethane, is essentially constant and therefore substitute in equation 1 the term $2\alpha(\text{Ethane})_T$ for the term $[R_3C]$. The halochromic salt is formed from the carbinol by the action of a proton

$$R_3COH + H^+ = R_3C^+ + H_2O \qquad (2)$$

The equilibrium constant for this reaction may be expressed by equation 3

$$K = \frac{[R_3COH]\,[H^+]}{[R_3C^+]\,[H_2O]} \qquad (3)$$

The concentration of total carbinol $[\text{Carb.}]_T$ is equal to $[R_3COH] + [R_3C^+]$ therefore substituting for $[R_3COH]$ in equation 3, the terms $[\text{Carb.}]_T - [R_3C^+]$ we obtain equation 3a

$$[R_3C^+] = \frac{[\text{Carb.}]_T\,[H^+]}{[H^+] + K[H_2O]} \qquad (3a)$$

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(1) THIS JOURNAL, 55, 3745 (1933).

(2) Conant, Small and Taylor, *ibid.*, 47, 1959 (1925).

Now making the appropriate substitutions in equation 1, we therefore arrive at the general equation 4

$$E_{\text{h}} = E_0 - \frac{RT}{F}\ln \alpha + \frac{RT}{F}\ln \frac{[\text{Carb.}]_{\text{T}}}{2[\text{Ethane}]_{\text{T}}} - \frac{RT}{F}\ln \frac{[\text{H}^+] + K[\text{H}_2\text{O}]}{[\text{H}^+]} \quad (4)$$

At constant volume we may consider that α is constant and set E_0' equal to $E_0 - RT \ln \alpha/F$. At constant hydrogen-ion activity and constant water content the potential of a solution in which $(\text{Carb.})_{\text{T}} = 2(\text{Ethane})_{\text{T}}$ may be called E_0''. It will be noted if the concentration of the reductant is expressed in terms of the dissociated compound that this would be an equimolecular mixture of oxidant and reductant. Inspection of the last term of equation 4 which contains the hydrogen-ion activity makes it evident that when the value of $K[\text{H}_2\text{O}]$ is much greater than (H^+) the value of E_0'' will be a linear function of the hydrogen-ion activity and $E_0'' = E_0' - (RT/F) \ln K(\text{H}_2\text{O})$. At the point where $K[\text{H}_2\text{O}]$ is less than (H^+) the potential will be independent of the hydrogen-ion activity and $E_0'' = E_0'$. There should thus be a sharp bend in the $E_0'' : (P\text{H})^{\text{HAc}}$ curve at a point corresponding to the change of the oxidant from being almost exclusively in the carbinol form to being almost exclusively in the halochromic ion form. Such breaks do occur as will be shown below.

The apparatus employed in measuring the oxidation–reduction potentials of the free radicals was identical with that used in the study of quinones and certain dyes. The potential was actually measured in every instance against a saturated aqueous calomel electrode and these readings were converted to the hydrogen electrode scale by adding 98 mv., which we have calculated in the previous paper to be the potential of the hypothetical hydrogen electrode against saturated calomel at $(P\text{H})^{\text{HAc}} = 0$. It is, of course, necessary that all the measurements be carried out in the complete absence of oxygen, as the free radicals react very rapidly with this gas. Three different methods were employed of varying the ratio of oxidant and reductant. In the method of mixtures a solution of the free radical in dry bromobenzene was placed in an atmosphere of oxygen-free nitrogen. Varying quantities of such a solution were then added to the glacial acetic acid buffer which contained a solution of the halochromic ion. The latter was usually formed by dissolving the corresponding carbinol directly in the buffer solution. Varying quantities of the reductant (the free radical) were added and the potential measured. Bright platinum electrodes were used in all of the work. Two titration methods were also employed. In one of these the halochromic salt solution was titrated with a chromous acetate. The other procedure depended on the fact that the indophenols in glacial acetic acid are much more powerful oxidizing agents than the halochromic salts. As a result it is possible to titrate the free radical with a solution of the oxidized form of indophenol dye. A very satisfactory end-point can be determined electrometrically, since there is a change of potential of some 200 mv. at the end-point. The end-point could also be estimated visually by the color change and these results always agreed satisfactorily with the electrometric end-point. In each experiment 5 cc. of buffer solution was employed; the concentration of carbinol and total reductant at the midpoint was usually about 0.001 molar.

To save space the three methods are illustrated by the three diagrams shown in Figs. 1, 2 and 3, illustrating, respectively, the method of mixtures (with a logarithmic plot of the ratio of oxidant to reductant), the titration of triphenylcarbinol with chromous acetate, and the titration of diphenyldixanthyl with indothymol. In each case the values plotted are E_0''.

The agreement between the method of mixtures and the titration methods was within the experimental error (10 millivolts). For example, with the triphenylmethyl system at $(P_H)^{HAc} = -0.98$, the method of mixtures yielded a value for E_0'' of 0.277 while the chromous acetate titration gave 0.277; with phenylxanthyl at $(P_H)^{HAc} = +0.24$, E_0'' by mixtures was 0.098, by titration with indothymol +0.084. In the more acid solutions the potentials were not stable for any long period as there is, of course, a decomposition of the free radicals by the action of the acids present. The temperature was kept at 25 ± 1° by means of a jacket around the electrochemical cell through which water at a constant temperature was allowed to flow. In one experiment with the triphenylmethyl system at $(P_H)^{HAc} = -0.98$ it was found that an increase in temperature of 10° changed the potential less than 2 mv. It is therefore clear that the temperature coefficient of such a system is so small that the control of temperature is not a significant factor.

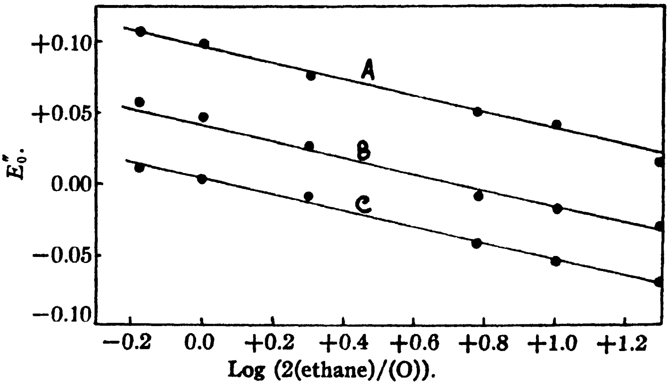

Fig. 1.—Potentials of diphenyldixanthyl by the method of mixtures: A at P_H +1.00, B at P_H +2.47, C at P_H +3.68. Lines were drawn with the theoretical slope.

In Fig. 4 are plotted all the final results with the three free radical systems which have been studied, namely, triphenylmethyl, phenylxanthyl and benzylxanthyl. The values plotted are those of E_0'' *vs.* $(P_H)^{HAc}$ the ionic strength of all the buffers was 0.2. The various symbols show whether the results were obtained by the method of titration or the method of mixtures. It will be seen that the agreement between the two methods is all that could be expected considering the difficulties of handling the free radicals and non-aqueous solutions.

The concentration of water in our solutions we estimate to be about 0.006 molar, due primarily to the water formed in the neutralization of the added carbinol. This is essentially the water concentration in previous work of Conant and Werner[3] on the basic strength of the carbinols and therefore their values of (pK) are directly comparable with those in this paper. We have measured the value of pK' of benzylxanthydrol by

[3] Conant and Werner, This Journal, 52, 4436 (1930).

titration at μ = 0.2 following the previous method and found a value of +0.70. The values of $pK' = -\log K(\mathrm{H_2O})$ for the three carbinols studied are therefore $(C_6H_5)_3COH$, −1.47, $C_6H_5COH(C_6H_4)_2O$, +1.91, $C_6H_5CH_2$-$COH(C_6H_4)_2O$, +0.70. The inflection of the E_0'' vs. $(P\text{H})^{\text{HAc}}$ curve of Fig. 4 should occur at the corresponding values of $(P\text{H})^{\text{HAc}}$. The points are indicated by the arrows. It is evident that in the case of the benzylxanthydrol system, the inflection occurs at exactly the right point; in the case of the phenylxanthydrol system there is a discrepancy of about 0.25 of a *P*H unit, which is about the experimental uncertainty. Unfortunately we were unable to obtain satisfactory potentials with the triphenylmethyl system in solutions sufficiently acid to give a fair test of the relation between theory and experiment in this instance. It may be that the E_0'' vs. $(P\text{H})^{\text{HAc}}$ curve becomes flat between $(P\text{H})^{\text{HAc}}$ = 0 and −1, but we believe that it is more probable that the point at −1 is in error and the curve takes the course shown in Fig. 4.

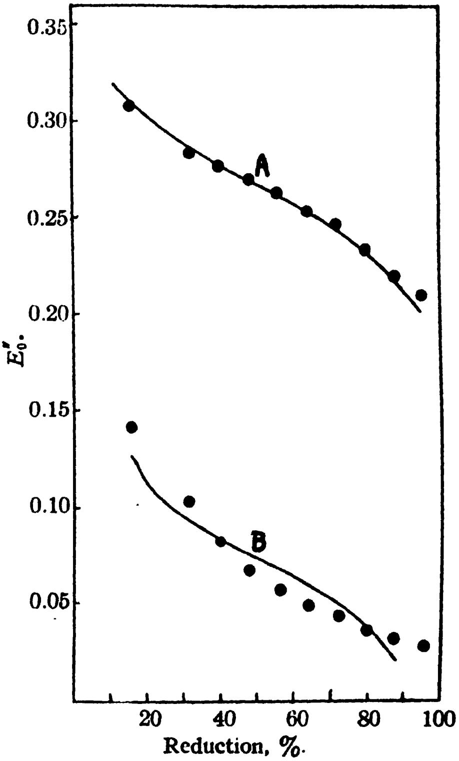

Fig. 2.—Reduction of triphenylcarbinol with chromous acetate. Theoretical curves were drawn through average E_0'': A at *P*H = 0.97, B at *P*H = +3.64.

The horizontal portions of the curves in Fig. 4 correspond to the value of E_0'; corrected for the value of α these give values of E_0 which is a measure of ΔF for the reduction of the halochromic ion to the free radical. The value of ΔF for the reduction of the carbinol to the free radical and water (in acetic acid at 0.006 *M* in water) can be calculated from this value and the term $-RT \ln K[\mathrm{H_2O}]$. (These values correspond to the intercept of the diagonal lines with the $(P\text{H})^{\text{HAc}}$ = 0 axis when the correction for α is duly applied.) In Table I we have summarized the values of ΔF expressed in volt electrons and for comparison the values of ΔF of dissociation of the ethane (the associated free radical). The data necessary for estimating α are indicated in the footnote of the table. The change of volume during an experiment would affect α in the case of triphenylmethyl and benzylxanthyl but we have calculated that the maximum change is not more than 14 mv. over the whole range; the values used in calculating the data in Table I correspond to the midpoint. Probably some of the discrepancies illustrated by the data in Figs. 1–3 are due to the change of α during the experiment but it did not seem worth while to carry out the calculations to make the necessary corrections.

TABLE I

FREE ENERGY OF REDUCTION OF HALOCHROMIC CARBINOLS TO FREE RADICALS

Carbinol	E_0'	Estimated α at dilution of expt.	ΔF of reduction of halochromic ion, E_0	ΔF of reduction of carbinol, E_0	ΔF of dissociation of ethane
$(C_6H_5)_3COH$	+0.315	0.38	+0.290	+0.225	−0.26
$(C_6H_5COH(C_6H_4)_2O$	+0.095	.92	+ .095	+ .175	− .16
$C_6H_5CH_2COH(C_6H_4)_2O$	+ .150	5×10^{-3}	− .062	− .017	− .50

The value of α for hexaphenylethane was taken from Ziegler's data;[4] the value for phenylxanthyl and benzylxanthyl from calculations appearing in another paper from this Laboratory. In this paper the value of ΔF of dissociation of these compounds is also estimated. The values of ΔF in columns 3, 4 and 5 correspond, respectively, to the processes

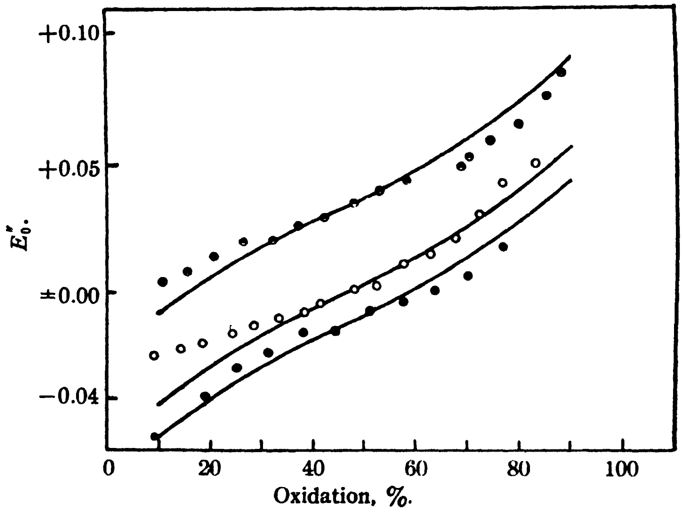

Fig. 3.—Oxidation of diphenyldixanthyl with indothymol. Theoretical curves were drawn through the average E_0'. A at P_H +2.47, B at P_H +3.68, C at P_H +4.24.

$$R_3C^+ + {}^1/_2H_2(\text{gas}) \longrightarrow R_3C + H^+ \text{ (at } (P_H)^{HAc} = 0) \qquad \text{(a)}$$

$$R_3COH + {}^1/_2H_2(\text{gas}) \longrightarrow R_3C + H_2O \text{ (in a 0.006 } M \text{ soln. in HAc)} \qquad \text{(b)}$$

$$R_3C\text{—}CR_3 \longrightarrow 2R_3C \qquad \text{(c)}$$

An inspection of the results shows that the free energies of reactions (a) and (c) are influenced to a greater degree by changes in structure than are the

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(4) Ziegler, *Ann.*, **473**, 163 (1929).

values for reaction (b). In even this latter case, however, there is a difference of 0.242 volt (the corresponding extreme difference for reaction (a) is 0.350 volt). The orders of the three compounds for reactions (a) and (b) are the same but clearly bear no relation to the free energy of dissociation (reaction c). At first sight it is surprising that there should be greater differences in the free energy of reduction of the ion than the carbinol in a series of compounds, particularly in view of the work of Bent,[5] which has shown that the affinity of free radicals for an electron is relatively little influenced by changes in structure. It seems probable that the explanation is due to the fact that in the case of the xanthyl ions, the halochromic ion is in part in the oxonium form (A). This ion cannot be reduced to a free radical only as a result of an electronic rearrangement. The relatively extreme basicity of the xanthyl compounds is, of course, merely another reflection of this same tendency. The few results obtained in our preliminary paper with the free radical from the very basic $C_6H_5COH(C_6H_4OCH_3)_2O$ indicate that the value for ΔF of reduction of the ion would here be even much more divergent from the value for the reduction of the carbinol. This compound is too basic to measure in glacial acetic acid. It would be a matter of considerable interest to measure the potentials of the free radicals from this compound and other very basic carbinols such as trianisylcarbinol in a series of non-aqueous buffers in such a solvent as butyl carbitol, and it is hoped that this may be soon accomplished. Such results would provide a drastic test of the hypothesis offered above.

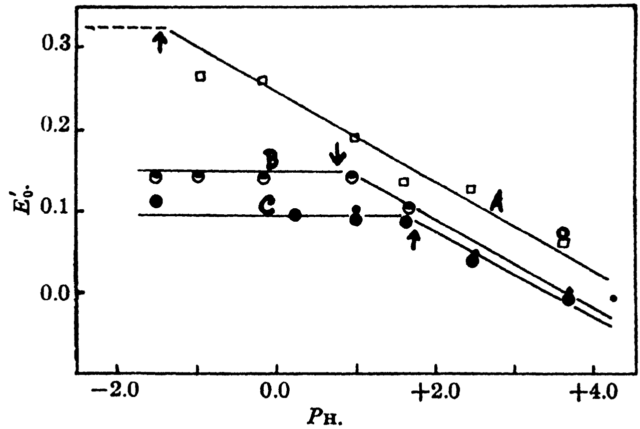
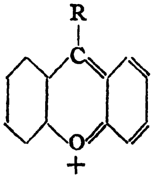


Fig. 4.—Change of $E_h^{0\prime}$ with the change of Pн. A for triphenylmethyl, B for benzylxanthyl, C for phenylxanthyl. Curves were drawn with the theoretical slope. Points in circles were obtained by titration.



A

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(5) Bent, THIS JOURNAL, 52, 1498 (1930); 53, 1786 (1931).

In conclusion we may point out an interesting consequence of the low oxidation–reduction potential of the free radical and the relatively high oxidation–reduction potential of the indophenol dyes. The free radical is oxidized by the dye to the corresponding halochromic ion (or, at the proper acidities, to the corresponding carbinol). As a result it is possible to titrate a free radical with indothymol. An excess of the dye is employed in a solution of acetic acid and bromobenzene. The excess of dye is then titrated with an aqueous solution of sodium thiosulfate. It was proved conclusively that these dyestuffs are quantitatively reduced by sodium thiosulfate according to the equation

$$\underset{\text{(indophenol)}}{A} + 2R_3C + 2H^+ \longrightarrow \underset{\text{(reduced indophenol)}}{AH_2} + 2R_3C^+ \text{ (or } R_3COH)$$

The titration of the dye with sodium thiosulfate was shown to correspond to the reaction

$$A + Na_2S_2O_3 + H_2O \longrightarrow AH_2 + Na_2SO_4 + S$$

A typical experiment was as follows: 2 cc. of a 0.006 *M* indothymol solution in acetic acid (glacial) was placed in a 50-cc. flask containing 1 cc. of bromobenzene. A weighed sample of free radical was introduced into the flask in a carbon dioxide atmosphere. After a few moments' agitation, 3 cc. of water was added and the excess of dye with thiosulfate; 2.329 mg. of diphenyldixanthyl required 0.834 cc. of 0.00926 *N* $Na_2S_2O_3$ for the back titration as compared with 1.318 cc. required by 2 cc. of the dye without addition of the free radical. Purity of diphenyldixanthyl 99%; by oxygen absorption in bromobenzene the purity was 98%.

The purity of the triphenylmethyl (hexaphenylethane) and the other free radicals used in this work were checked by oxygen absorption measurements in bromobenzene or by titration with indothymol. Since these free radicals have been prepared repeatedly in many laboratories, we will not take the space to detail their preparation in this paper. In all cases the purity was at least 98% as determined by one of the two methods.

Summary

The oxidation–reduction potentials of three free radicals and their halochromic salts have been measured in glacial acetic acid solutions. The changes of potential with changes in acidity of the buffer solutions are in accord with the theory developed in a preliminary paper.

CAMBRIDGE, MASSACHUSETTS

RECEIVED MAY 12, 1933
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[CONTRIBUTION NO. 19 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Monoarylguanidines. IV. Benzoselenazoleguanidine[1,2]

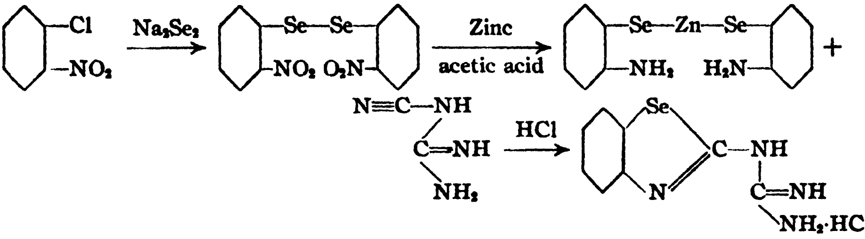
BY G. B. L. SMITH, J. P. MIALE AND C. W. MASON[3]

Introduction

In previous communications[1b,1c] it has been shown that dicyandiamide reacts with *o*-aminophenol and *o*-aminothiophenol to form benzoxazoleguanidine and benzothiazoleguanidine. Since the analogy existing in organic chemistry between selenium on the one hand, and oxygen and sulfur on the other, is well established for many types of compounds, the preparation of benzoselenazoleguanidine by the analogous reaction of dicyandiamide with *o*-aminoselenophenol should be possible.

This investigation was undertaken in order that the physical, chemical, and pharmacological properties of benzoselenazoleguanidine might be studied and compared with those of the oxy, thio and imide analogs. The present paper describes a further application of the nitrile property of dicyandiamide in its reaction with *o*-aminoselenophenol to form benzoselenazoleguanidine.

Properties of Benzoselenazoleguanidine.—The synthesis of benzoselenazoleguanidine was accomplished through the reaction series



Benzoselenazoleguanidine is a white crystalline solid resembling macroscopically the hydrated needles of benzothiazoleguanidine[1c] but it is not hydrated. It is only sparingly soluble in water and its aqueous solution is a weak base comparable in strength with the other analogs. This is shown by the potentiometric titration and the fact that the salts of benzoselenazoleguanidine and strong acids may be titrated with a standard solution of sodium hydroxide, using phenolphthalein as indicator.[4]

In another respect the salts are like those of the thio and oxy compounds, the picrate being the least soluble and the hydrochloride the most soluble.

(1) For earlier articles of the series see (a) Smith, THIS JOURNAL, **51**, 476 (1929); (b) Smith, Kane, and Mason, *ibid.*, **51**, 2522 (1929); (c) Smith, Mason, and Carroll, *ibid.*, **53**, 4103 (1931).

(2) The substances described were prepared by Mr. Miale and this paper is an abstract of part of the thesis submitted by him in partial fulfilment of the requirements for the degree of Bachelor of Science in Chemistry at the Polytechnic Institute of Brooklyn in June, 1932.

(3) Assistant Professor of Chemical Microscopy at Cornell University.

(4) The titration curve will be given in an article on base strength of some arylbiguanidines and related compounds soon to be published from this Laboratory.

For the series, the order of solubility of their salts in aqueous solution from most soluble to least soluble is as follows: hydrochloride—thio, seleno, oxy; sulfate—seleno, oxy, thio; nitrate—oxy, thio, seleno; picrate—oxy, seleno, thio; and of the base—thio, oxy, seleno. A comparison of the melting points of the several compounds[1b,1c] likewise fails to show any strict periodic relationships among them.

Experimental

Materials.—*The zinc salt of o-aminoselenophenol* was prepared by reducing *o*-dinitrodiphenyl diselenide with zinc in a solution of glacial acetic acid.[5] *o*-Dinitrodiphenyl diselenide was prepared by the method of Bogert and Anderson[5] as modified by Bogert and Stull,[6] which consisted of the interaction of sodium diselenide[7] with *o*-nitrochlorobenzene.[8]

Benzoselenazoleguanidine Hydrochloride.—Dicyandiamide (approx. 2 g.) and zinc *o*-aminoselenophenol (approx. 2 g.) were dissolved in 200 ml. of water and heated to boiling under a reflux. A dilute solution of hydrochloric acid was added slowly in very slight excess and the heating was continued for about three hours. There was a slight odor of hydrogen selenide and a small amount of elementary selenium separated. The solution was then filtered and decolorized with Norit, and after making strongly acid with hydrochloric acid (50 ml. of solution and 5 ml. of concd. hydrochloric acid), was allowed to stand for twelve hours. The hydrochloride separated as a white microcrystalline precipitate, which was filtered, washed with alcohol and dried.

Benzoselenazoleguanidine (Base).—One gram of benzoselenazoleguanidine hydrochloride was dissolved in 20 ml. of hot water and a slight excess of a 20% solution of sodium hydroxide was added. The base separated immediately and was filtered, washed with cold water and dried.

Benzoselenazoleguanidine Sulfate, Nitrate and Picrate.—The sulfate, nitrate and picrate were obtained by adding a solution of the respective acid to a solution of benzoselenazoleguanidine hydrochloride obtained as described above and in each case an immediate precipitation of the salt resulted. The substances were filtered, washed with cold water and dried. The nitrate and sulfate were white microcrystalline solids and the picrate was yellow. Analytical and other data concerning benzoselenazoleguanidine and its salts are given in Table I.

Microscopical Studies

Benzoselenazoleguanidine.—As prepared macroscopically there is no evidence of decomposition and coarse prisms, roughened by transverse striations, but otherwise transparent, are observed. When recrystallized from aqueous alcohol either thin plates and skeletal leaflets, or, if cooled very slowly, tabular crystals, rectangular or with terminal angles of about 140°, are formed. These crystals are biaxial and have their axial plane lengthwise, with the acute bisectrix inclined to the principal pinacoidal faces; they are in all probability monoclinic. Double refraction is strong, positive (+), with $2V$ about 30° and $r > v$ very strong. Refractive indices of the pinacoidal views are: vibrations crosswise, 1.780 (±0.005);

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(5) Bogert and Anderson, *Proc. Nat. Acad. Sci.*, **11**, 217 (1925).

(6) Bogert and Stull, This Journal, **49**, 2011 (1927).

(7) Sodium selenide was purchased from Eimer and Amend.

(8) Purchased from the Eastman Kodak Company.

TABLE I

ANALYTICAL AND OTHER DATA OF BENZOSELENAZOLEGUANIDINE AND ITS SALTS

Compound	M. p., °C.	Analyses, %				Soly. at 20° g./100 g. of H_2O	Solubility in non-aqueous solvents
			Calcd.	Found			
Base	198–200	C	40.13	40.08	39.94	0.0134	Insol. CS_2, $CHCl_3$, Bz; sol. EtOH, Et_2O, acetone
		H	3.34	3.38	3.68		
Nitrate	193–198	C	31.77	31.89		0.0388	Insol. Et_2O, Bz, CS_2, $CHCl_3$; sl. sol. EtOH; sol. acetone
		H	3.00	3.26			
		HNO_3	20.84	20.74			
Hydrochloride	247–249	C	34.81	34.83		1.9114	Insol. $CHCl_3$, Bz; sl. sol. CS_2, EtOH, Et_2O; sol. acetone
		H	3.29	3.26			
		N	20.30	19.36			
Sulfate	287–289	C	33.29	32.89		0.3891	Insol. Et_2O, Bz, CS_2, $CHCl_3$; sl. sol. EtOH, acetone
		H	2.95	3.42			
		Se	27.47	27.63	27.50		
Picrate	267–270	C	35.88	35.86		0.0316	Insol. Et_2O, CS_2, $CHCl_3$; sl. sol. EtOH, Bz, acetone
		H	2.36	2.59			
		N	20.90	20.99			

lengthwise, 1.640 (±0.005); crystals on edge exhibit another value for vibrations crosswise, 1.9 (est.). From the melt spherulites of fine leaflets are obtained and there is no evidence of decomposition before melting.

Benzoselenazoleguanidine Hydrochloride.—Prisms with numerous lengthwise striations and inclusions are observed in the original sample of the material. On recrystallization from water well-formed prisms (110), of orthorhombic symmetry, with basal (001) and macro (100), pinacoidal faces also prominent are observed. All views give parallel extinction; $Bx_a = C$; axial plane $\perp$ b; $2V$ is large, $r > v$, and double refraction negative (−). Refractive indices are $\alpha = 1.580$ (±0.005); $\beta = 1.785$ (±0.005); $\gamma = 2.0 +$ (est.). $X = c$, $Y = b$, $Z = a$. From a fused melt there are obtained monoclinic prisms with clinopinacoid, analogous in form to those similarly obtained from benzothiazoleguanidine hydrochloride. They show an extinction angle of about 15°, strong positive (+) double refraction, and Bx_a nearly $\perp$ to (001).

Benzoselenazoleguanidine Sulfate.—The substance appears as thin rectangular plates, usually nearly square, and as platy rosets. The crystals are uniaxial, optically positive (+) and belong to the tetragonal system. Refractive indices are, ω 1.615 (±0.005), ϵ 1.83 ± 0.1.

Benzoselenazoleguanidine Nitrate.—Either as originally prepared or as recrystallized from water, thin prisms are observed. The crystals are of monoclinic symmetry, elongated // c with clinopinacoidal faces prominent; the angle β is about 75°. Views showing parallel extinction have refractive indices of 1.480 (±0.005) for vibrations lengthwise and 1.87 (±0.1) for vibrations crosswise. Views showing oblique extinction have refractive indices of 1.460 (±0.005) for vibrations 18° to their elongation and 1.81 (±0.01) for vibrations $\perp$ to this direction. 2 V is about 60°, and double refraction is negative (−). The axial plane is // b, with Bx_a visible in end views.

Benzoselenazoleguanidine Picrate.—Yellow needles with faint if any pleochroism appear in recrystallization from water. Extinction is either parallel or about 18°. Refractive indices are: vibration crosswise, *ca.* 1.9; vibrations lengthwise, 1.495 (±0.005). The crystals are probably monoclinic.

Summary

The benzazoleguanidine series has been extended by the preparation of benzoselenazoleguanidine through the reaction between dicyandiamide and *o*-aminoselenophenol. The base, nitrate, hydrochloride, sulfate and picrate have been isolated and certain physical, chemical and crystallographical properties of these substances have been observed.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Studies of Conjugated Systems. XIV. The Preparation and Properties of 1-Phenyl-4-aminobutadiene and 1-Phenyl-4-anilidobutadiene

BY IRVING E. MUSKAT AND LOREN B. GRIMSLEY

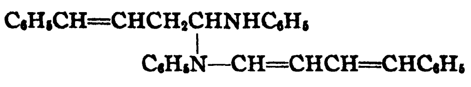
The characteristic properties and addition reactions of conjugated systems have been for some time the subject of an investigation in this Laboratory. One of the objects of this investigation was to throw some light on the mechanism of substitution and directive influence in the aromatic series. Some of the addition reactions of butadiene, phenylbutadiene, carboxybutadiene, chloro- and bromobutadiene have already been studied and a theory has been developed[1] which explains these addition reactions without recourse to any special hypothesis of conjugation. In this paper we shall present the results of an investigation on the preparation and properties of aminobutadiene derivatives.

The aminobutadiene derivatives are the aliphatic analogs of the aromatic amines, such as aniline, diphenylamine and α-naphthylamine. Since the aromatic amines are among the most reactive as well as among the most important of aromatic compounds, a study of the aminobutadiene derivatives may not only throw some light on the reactions of aromatic

[1] Muskat and Northrup, THIS JOURNAL, 52, 4043 (1930).

amines, but may also prove of considerable interest for synthetic work. For instance, the diazotization and subsequent coupling reactions of these aminobutadiene derivatives would lead to a most interesting group of compounds. The aminobutadiene derivatives selected for this study were 1-phenyl-4-anilidobutadiene and 1-phenyl-4-aminobutadiene.

The 1-phenyl-4-anilidobutadiene was prepared by treating 1-phenyl-4-bromobutadiene with aniline. This reaction was carried out in various solvents in order to determine the conditions for optimum yield of the amine. It was found that the best yield was obtained when aniline was used as the solvent. The amine could not be distilled even under reduced pressure; there remained in the distilling flask a dimer of the amine which readily forms a monohydrochloride salt. No effort was made to prove the structure of this dimer but the formula given is suggested. This formula would account for the fact that only the monohydrochloride salt of the dimer is formed.



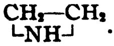
$$\begin{array}{l} C_6H_5CH{=}CHCH_2CHNHC_6H_5 \\ \qquad\qquad\qquad\quad | \\ C_6H_5N{-}CH{=}CHCH{=}CHC_6H_5 \end{array}$$

The reactions of this amine were then studied. When dry hydrogen chloride is passed into an anhydrous ether solution of the amine, the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene is precipitated. This salt hydrolyzes when exposed to the atmosphere. When dry benzene is used as the solvent in place of ether, the dihydrochloride of 1-phenyl-4-anilidobutadiene is formed. This compound is the hydrogen chloride salt of what is probably 1-phenyl-3-chloro-4-anilido-Δ^1-butene. This salt hydrolyzes only very slowly when exposed to the atmosphere. The 1-phenyl-3-chloro-4-anilido-Δ^1-butene was treated with an excess of chlorine in chloroform solution. 1-Phenyl-1,2,3-trichloro-4-trichloroanilidobutane hydrochloride was formed.

It was further found that the 1-phenyl-4-anilidobutadiene readily absorbs one mole of bromine to give 1-phenyl-3,4-dibromo-4-anilido-Δ^1-butene. The structure of this compound was determined by ozonolysis. This dibromide absorbs a second mole of bromine to give 1-phenyl-1,2,3,4-tetrabromo-4-anilidobutane. On further treatment with an excess of bromine, 1-phenyl-1,2,3,4-tetrabromo-4-tribromoanilidobutane hydrobromide was formed. The 1-phenyl-4-anilidobutadiene absorbs likewise a mole of chlorine to give 1-phenyl-3,4-dichloro-4-anilido-Δ^1-butene. The hydrogen chloride salt was precipitated when dry hydrogen chloride was passed into an ethereal solution of the dichloride.

The 1-phenyl-4-aminobutadiene was prepared by the interaction of alcoholic ammonia with 1-phenyl-4-bromobutadiene. An attempt to distil the amine under reduced pressure was not successful. When dry hydrogen chloride is passed into an ether solution of the amine, the hydrogen chloride salt is formed. This salt hydrolyzes when exposed to the atmosphere. If dry benzene is used as the solvent in place of the ether, the hydrochloride salt of what is probably 1-phenyl-3-chloro-4-amino-Δ^1-butene is formed. This salt is hydrolyzed only very slowly under similar conditions.

It was likewise found possible to prepare the 1-phenyl-4-aminobutadiene by the reaction of sodium or potassium amide in liquid ammonia solution upon 1-phenyl-4-bromobutadiene, and also by the reaction of potassium phthalimide upon 1-phenyl-4-bromobutadiene, followed by the hydrolysis of the resulting product. It was further found possible to bring about the rearrangement of the acid amide of styrylacrylic acid to 1-phenyl-4-aminobutadiene by heating it with an aqueous solution of sodium hypochlorite.[2]

It is interesting to note that both the 1-phenyl-4-aminobutadiene and 1-phenyl-4-anilidobutadiene are stable in the amino form rather than in the imino form. This seems to emphasize the rather close analogy between the aliphatic conjugated compounds and aromatic compounds. Every effort to prepare aliphatic amines in which the amino group is attached to an unsaturated carbon atom has always yielded the corresponding imino derivatives or cyclic derivatives.[3] In the case of vinylamine, there is some question as to its true structure. Gabriel,[4] who first synthesized it, gave its structure as $CH_2{=}CHNH_2$. This was later disproved by Marckwald[3] who favored the cyclic structure,  $\underset{\llcorner NH \lrcorner}{CH_2{-}CH_2}$. A number of the unsaturated amino derivatives have been given the imide structure, $RCH_2CH{=}NH$.[3] However, the 1-phenyl-4-aminobutadiene and 1-phenyl-4-anilidobutadiene are stable in the amino form just as is aniline. A number of attempts were made to hydrolyze both these amines but in no case were we able to detect ammonia or aniline in the hydrolytic products. The addition reactions of the 1-phenyl-4-anilidobutadiene and of 1-phenyl-4-aminobutadiene eliminate the possibility of the cyclic structure.

Experimental Part

1-Phenyl-4-anilidobutadiene.—1-Phenyl-4-bromobutadiene prepared according to the method of Muskat and Grimsley[5] was treated with a large excess of aniline and allowed to stand at room temperature for twenty-four hours. The excess aniline was removed by treating with cold dilute hydrochloric acid. The resulting mixture was extracted several times with ether, the ether extract dried over anhydrous sodium sulfate and then over sodium hydroxide. The ether solution was filtered from the sodium hydroxide and dry hydrogen chloride was passed into the filtrate. A slightly yellow, crystalline precipitate was formed. The crystals were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride, and then dried in a vacuum desiccator over phosphorus pentoxide. These crystals melted at 104–106° and hydrolyzed when exposed to the atmosphere. Due to this hydrolysis, the melting point may be somewhat low. The maximum yield, based upon the amount of the 1-phenyl-4-bromobutadiene which reacted, was 57%.

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(2) The relation of these studies on the reactions of conjugated amines to the problem of substitution in the benzene ring will be discussed in a later paper.

(3) Marckwald, *Ber.*, **33**, 764 (1900); Howard and Marckwald, *ibid.*, **32**, 2031 (1899); Kohler and Drake, THIS JOURNAL, **45**, 1287 (1923).

(4) Gabriel, *Ber.*, **21**, 1049 (1888); Gabriel and Stelzner, *ibid.*, **28**, 2929 (1895).

(5) Muskat and Grimsley, THIS JOURNAL, **55**, 2860 (1933).

Anal. Calcd. for $C_{16}H_{16}NCl$: Cl, 13.74. Found: Cl, 13.81, 13.91.

This chlorine analysis indicates that the compound is the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene.

The hydrogen chloride salt of 1-phenyl-4-anilidobutadiene was hydrolyzed with dilute aqueous alkali and the resulting mixture was extracted with ether. The ether solution was washed free of chloride ion and then dried first over anhydrous sodium sulfate and finally over sodium hydroxide. The ether was removed by means of suction. The free base, a dark red viscous oil, remained.

Anal. Calcd. for $C_{16}H_{15}N$: N, 6.33. Found: N, 6.21, 6.26.

These analyses show that the compound is 1-phenyl-4-anilidobutadiene.

1-Phenyl-4-chlorobutadiene, prepared according to the method of Muskat and Huggins,[6] was treated with aniline in a manner exactly analogous to that described above for the corresponding bromo derivative. The hydrogen chloride salt of the anilide thus obtained was identical with the 1-phenyl-4-anilidobutadiene hydrochloride whose preparation from 1-phenyl-4-bromobutadiene was described above. Since the monochloride was definitely proved[6] to have the structure $C_6H_5CH{=}CHCH{=}CHCl$, this constitutes definite proof of the similar structure of the corresponding monobromide.

An attempt to distil, under reduced pressure, the 1-phenyl-4-anilidobutadiene was not successful but there remained in the distilling flask a red rosin-like solid which was easily pulverized into an orange powder. This powder melted at 105°.

Mol. wt. Calcd. for $(C_{16}H_{15}N)_2$: mol. wt., 442. Found: mol. wt. (freezing point method, benzene), 446.

The powder was dissolved in benzene and dry hydrogen chloride was passed into the solution; a crystalline precipitate was formed. The crystals were collected on a filter by means of suction and washed with dry ether to remove the excess hydrogen chloride. These crystals melted at 152°.

Anal. Calcd. for $(C_{16}H_{15}N)_2HCl$: Cl, 7.41. Found: Cl, 6.80, 6.89.

Reactions of 1-Phenyl-4-anilidobutadiene

Addition of Hydrogen Chloride.—The 1-phenyl-4-anilidobutadiene was dissolved in dry benzene and dry hydrogen chloride passed into the solution while the container was immersed in an ice-bath. The solution became dark red in color but no precipitate was formed. Dry, low boiling ligroin (30–60°) was added dropwise to the solution and a chocolate brown crystalline material was precipitated. These crystals were collected on a filter by means of suction and washed with a small amount of warm benzene. The crystals which remained were slightly pink in color.

Anal. Calcd. for $C_{16}H_{17}NCl_2$: Cl, 24.12. Found: Cl, 24.03, 23.93.

The compound is the dihydrochloride of 1-phenyl-4-anilidobutadiene.

In order to determine the ionizable chlorine, the compound was dissolved in alcohol. An equal volume of water was added to precipitate the organic residue, and immediately filtered to avoid the hydrolysis of any loosely bound organic chlorine. The chloride ion was determined in the filtrate.

Anal. Calcd. for one ionizable chlorine in $C_{16}H_{17}NCl_2$: Cl, 12.06. Found: Cl, 12.58.

The compound is then the hydrogen chloride salt of the monohydrochloride addition product of 1-phenyl-4-anilidobutadiene.

These crystals melted at 124° and were hydrolyzed in contact with the atmosphere, but not as readily as was the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene. The crystals are soluble in alcohol, acetone, chloroform, and to quite an appreciable extent in hot benzene.

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[6] Muskat and Huggins, THIS JOURNAL, 51, 2496 (1929).

This dihydrogen chloride derivative of 1-phenyl-4-anilidobutadiene was dissolved in chloroform and a current of ozonized oxygen passed into the solution for about twenty-four hours. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The hydrogen chloride has therefore been absorbed in the 3,4-positions of the 1-phenyl-4-anilidobutadiene. We did not determine the orientation of the hydrogen chloride in the 3,4-double bond but due to its reactions and also upon theoretical grounds we favor the formula 1-phenyl-3-chloro-4-anilido-Δ^1-butene. In what follows, we shall use this formula although its structure was not proved.

The 1-phenyl-3-chloro-4-anilido-Δ^1-butene hydrochloride was dissolved in chloroform, and a current of chlorine was passed into the solution until no more was absorbed. The chloroform was removed by means of suction. There remained a residue of slightly yellow crystals which were washed with ether to remove the color. The pure white crystals melted at 218°

Anal. Calcd. for $C_{16}H_{14}NCl_7$: Cl, 53.00 Found: Cl, 53.17, 53.08.

The compound is 1-phenyl-1,2,3-trichloro-4-trichloroanilidobutane hydrochloride.

Addition of Bromine.—The 1-phenyl-4-anilidobutadiene was dissolved in chloroform and exactly one mole of bromine, dissolved in chloroform, was added. After the reaction was complete, the chloroform was removed by means of suction. There remained a dark purple colored solid, which when pulverized was dark brown in color This compound melted at 103°.

Anal. Calcd. for $C_{16}H_{15}NBr_2$: Br, 42.22. Found: Br, 42.25, 42.41.

This analysis shows the compound to be the dibromide of 1-phenyl-4-anilidobutadiene.

The dibromide was dissolved in chloroform and a current of ozonized oxygen passed into the solution for about twenty-four hours. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The compound thus proves to be 1-phenyl-3,4-dibromo-4-anilido-Δ^1-butene.

The 1-phenyl-3,4-dibromo-4-anilido-Δ^1-butene was dissolved in chloroform and exactly one mole of bromine, dissolved in carbon tetrachloride was added. When the raction was complete, the chloroform and the carbon tetrachloride were removed by means of suction and a purple crystalline residue remained.[7]

Anal. Calcd. for $C_{16}H_{15}NBr_4$: Br, 59.14. Found: Br, 58.94, 58.92.

The compound is the tetrabromide of 1-phenyl-4-anilidobutadiene.

The tetrabromide of 1-phenyl-4-anilidobutadiene was dissolved in chloroform and quite an excess of bromine, dissolved in carbon tetrachloride, added. The reaction mixture was allowed to stand at room temperature for about forty-eight hours. Large volumes of hydrogen bromide were evolved and crystals separated out. The crystals were collected on a filter by means of suction and washed with small amounts of chloroform. The pure white crystals which remained melted at 182°.

Anal. Calcd. for $C_{16}H_{13}NBr_8$: Br, 74.50. Found: Br, 74.62, 74.70.

The compound is the hydrogen bromide salt of 1-phenyl-1,2,3,4-tetrabromo-4-tribromoanilidobutane.

Addition of Chlorine.—The 1-phenyl-4-anilidobutadiene was dissolved in chloroform and exactly one mole of chlorine, dissolved in chloroform, was added. The re-

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(7) These crystals melted at 88-91°. Judging from the melting point of similar compounds described above, this melting point may be low.

action mixture was allowed to stand at room temperature for about twenty-four hours. The chloroform was removed by means of suction and the dark red viscous oil remaining was taken up in dry ether. The solution was filtered clear and the ether was removed from the filtrate by means of suction. The dark red viscous oil which remained was analyzed for chlorine.

Anal. Calcd. for $C_{16}H_{15}NCl_2$: Cl, 24.28. Found: Cl, 24.10, 24.12.

The compound is the dichloride of 1-phenyl-4-anilidobutadiene.

The dichloride of 1-phenyl-4-anilidobutadiene was dissolved in dry ether and dry hydrogen chloride was passed into the solution. The crystals which precipitated out were almost pure white. They were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride and then dried in a vacuum desiccator over anhydrous calcium chloride. The crystals melted at 135°.

Anal. Calcd. for $C_{16}H_{16}NCl_3$: Cl, 32.39. Found: Cl, 32.55, 32.59.

The compound is the hydrogen chloride salt of the dichloride of 1-phenyl-4-anilidobutadiene.

These crystals were dissolved in chloroform and a current of ozonized oxygen passed into the solution. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The compound is therefore 1-phenyl-3,4-dichloro-4-anilido-Δ^1-butene hydrochloride.

1-Phenyl-4-aminobutadiene.—The 1-phenyl-4-bromobutadiene was dissolved in alcohol and gaseous ammonia passed into the solution for about three days. The reaction product was diluted with a large volume of water and then extracted with ether. The ether extract was washed free of bromide ion and of ammonia and dried, first over anhydrous sodium sulfate, and then over sodium hydroxide. Dry hydrogen chloride was passed into the solution; a slightly yellow crystalline precipitate was formed. The passage of the hydrogen chloride into the solution was not carried out too long lest the salt of any secondary amine be likewise precipitated. The crystals were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride and then dried in a vacuum desiccator over phosphorus pentoxide. The crystals were slightly yellow and melted at 111°.

Anal. Calcd. for $C_{10}H_{12}NCl$: Cl, 19.53; N, 7.71. Found: Cl, 19.64, 19.70; N, 7.52, 7.61.

The compound is the hydrogen chloride salt of 1-phenyl-4-aminobutadiene.

The hydrogen chloride salt of 1-phenyl-4-aminobutadiene was dissolved in moist chloroform and a current of ozonized oxygen was passed into the solution. The chloroform was removed by means of suction and the residual ozonide decomposed with water. Benzoic acid was isolated from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid.

Addition of Hydrogen Chloride.—The 1-phenyl-4-aminobutadiene was dissolved in dry benzene and dry hydrogen chloride was passed into the solution. A precipitate was not formed but the solution became dark red in color. Low boiling ligroin was added, drop by drop, to the solution and a chocolate brown crystalline mass was precipitated. The crystals were washed with small quantities of warm benzene and then dried on a porous plate. The crystals were slightly pink in color and melted at 138°.

Anal. Calcd. for $C_{10}H_{13}NCl_2$: Cl, 32.54. Found: Cl, 32.41, 32.38.

The structure of the compound is assumed to be 1-phenyl-3-chloro-4-amino-Δ^1-butene hydrochloride for the same reasons as given above for 1-phenyl-3-chloro-4-anilido-Δ^1-butene.

The 1-phenyl-4-aminobutadiene was prepared also by the following methods. (a) An ether solution of 1-phenyl-4-bromobutadiene was introduced into a bomb tube and liquid ammonia condensed upon it. The tube was sealed and allowed to stand at room temperature for two or three days. The reaction product was worked up in a manner analogous to that described above. It was found that if sufficient alcohol were added to the tube to ensure a homogenous solution, the time of the reaction was materially shortened. It was likewise found that if the 1-phenyl-4-bromobutadiene was dissolved in alcohol, concentrated ammonium hydroxide added almost to the point of precipitating out the monobromide and the solution allowed to stand for about forty-eight hours, the 1-phenyl-4-aminobutadiene was formed.

(b) 1-Phenyl-4-bromobutadiene was dissolved in ether, a suspension of finely ground sodium amide in dry ether added and the mixture stirred mechanically. The reaction mixture was allowed to stand for eight to ten hours and the excess of sodium amide destroyed with moist ether. The reaction product was then diluted with an equal volume of ether and the solution was washed free of bromide ion and dried, first over anhydrous sodium sulfate and then over sodium hydroxide. Dry hydrogen chloride was passed into the solution and the hydrogen chloride salt of 1-phenyl-4-aminobutadiene was precipitated. Dry xylene was used to replace the ether in order that the temperature might be raised. The only result apparent was an increase in the polymerization.

The 1-phenyl-4-bromobutadiene was treated with sodium amide, dissolved in liquid ammonia, and the reaction mixture worked up as before. The 1-phenyl-4-aminobutadiene hydrochloride was isolated. Potassium amide was used with similar results.

(c) 1-Phenyl-4-bromobutadiene, in alcoholic solution, was treated with an alcoholic solution of potassium phthalimide and the reaction mixture allowed to stand at room temperature for about twenty-four hours. The reaction mixture was diluted with a large quantity of water and then extracted with ether. The ether extract was washed free of bromide ion and the ether was removed by gentle warming. The resulting residue was hydrolyzed with aqueous hydrochloric acid. The solution was then made alkaline with sodium hydroxide and extracted with ether. The ether solution was washed free of chloride ion and dried, first over anhydrous sodium sulfate and then over sodium hydroxide. 1-Phenyl-4-aminobutadiene hydrochloride was isolated from this solution.

(d) Styrylacrylic acid, $C_6H_5CH{=}CH{-}CH{=}CHCOOH$, was prepared according to the method of Doebner[8] by heating for six hours a mixture of 90 g. of cinnamic aldehyde, 90 g. of malonic acid, and 70 g. of pyridine and then pouring the reaction mixture into cold dilute sulfuric acid. The acid thus formed was purified by crystallization from dilute alcohol. The acid melted at 165°. The acid chloride of styrylacrylic acid was prepared according to the method of Rupe[9] by heating, the acid for forty minutes with an excess of phosphorus trichloride in the presence of a small amount of dry benzene. However, it was not found necessary to isolate the acid chloride. The benzene solution of the acid chloride was poured off. Concentrated ammonium hydroxide was added to the benzene solution and then gaseous ammonia was passed into the solution for about thirty minutes. The reaction vessel was immersed in an ice-bath during the reaction. The solid that was formed was collected on a filter by means of suction and washed several times with concentrated ammonium hydroxide in order to remove any unchanged acid. The crystals which remained melted at 185°, the melting point of the acid amide of styrylacrylic acid. These crystals, in aqueous suspension, were treated with a freshly prepared 8% solution of sodium hypochlorite and the reaction mixture heated on the water-bath for six hours. The reaction mixture was then extracted with ether and the solution washed free of chloride ion. It was then dried, first over anhydrous sodium sulfate and then over sodium hydroxide. Dry hydrogen chloride was passed into the

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(8) Doebner, *Ber.*, **35**, 2137 (1902).

(9) Rupe, *Ann.*, **369**, 340 (1909).

dry ether solution; the hydrogen chloride salt of 1-phenyl-4-aminobutadiene was precipitated from this solution. It is apparent that the acid amide of styrylacrylic acid has undergone a rearrangement to give 1-phenyl-4-aminobutadiene.

Summary

1. The method of preparation of 1-phenyl-4-aminobutadiene and of 1-phenyl-4-anilidobutadiene is described.
2. Both of these amines absorb hydrogen chloride in the 3,4-positions.
3. 1-Phenyl-4-anilidobutadiene absorbs both chlorine and bromine in the 3,4-positions.
4. The significance of these reactions of aliphatic amino conjugated compounds to the problem of substitution in the benzene ring is indicated.

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The Effects of Glucose and Fructose on the Sucrose Content in Potato Slices

BY J. M. NELSON AND R. AUCHINCLOSS

The opinion seems to be held by many[1] that desiccation of starch containing plant tissues, such as leaves and potato slices, increases the sucrose content. Schroeder and Horn[2] studying the increase in sucrose on drying tropæolum leaves as well as the changes in the amount of reducing sugar present in the leaves, reached the conclusion that starch is converted into sucrose in the desiccation of the leaves in a more direct way than through the reducing sugars as an intermediate stage. Ahrns[3] more or less repeated the work of Schroeder and his co-workers using starch bearing leaves of several plants, and also reached the conclusion that the conversion of the starch to sucrose in the desiccation of leaves is independent of the reducing sugars present.

Waterman[4] studied the phenomenon of starch to sucrose by drying potato slices at temperatures from 30 to 50°, and like the above-mentioned investigators expressed the opinion that starch is changed to sucrose during the drying process, in some direct way, probably by the aid of enzymic action. Following Waterman, de Wolff[5] studied the starch to sucrose reaction when potato slices are subjected to desiccation. He too looked upon the reaction as one independent of the reducing sugars present.

(1) M. W. Onslow, "The Principles of Plant Biochemistry," The University Press, Cambridge, 1931, p. 55; R. A. Gortner, "Outlines of Biochemistry," John Wiley and Sons, New York, 1929, p. 535.

(2) H. Schroeder and T. Horn, *Biochem. Z.*, **130**, 165 (1922); H. Schroeder and F. Herman, *ibid.*, **235**, 407 (1931).

(3) W. Ahrns, *Bot. Archiv.*, **5**, 234 (1924).

(4) H. I. Waterman, *Chem. Weekblad.*, **11**, 332 (1914).

(5) C. J. de Wolff, *Biochem. Z.*, **176**, 225 (1926); **178**, 36 (1926).

Contrary to the conclusions reached by Schroeder and his co-workers and by Ahrns, in the case of leaves, and also contrary to the view held by Waterman and de Wolff that starch is changed directly into sucrose when these plant tissues are dried, the results obtained in this Laboratory show that reducing sugars, in the form of glucose and fructose, play a dominating role in the formation of sucrose in potato slices, and that desiccation is only incidental. By dipping the slices in aqueous glucose or fructose solutions and then permitting them to remain in the moist condition, without any desiccation or loss of moisture whatever, in contact with air, even a larger increase in sucrose content results than when the slices are dried without dipping them in the hexose solution. The formation of sucrose by simply drying leaves and potato slices is probably also due to reducing sugars present in the tissue or formed during the desiccation.

In connection with the effect of reducing sugars on the sucrose content of potato slices it was found that slices dipped in galactose, maltose or glycerin solutions instead of glucose or fructose solutions showed only a small increase in sucrose. Similarly freshly cut slices, dipped in distilled water, instead of in a glucose solution, or not dipped at all, when exposed in the wet condition to air gave only slight increases in sucrose. These small increases are very likely due to wounding. Hopkins[6] has shown that when potato tissues are wounded by cutting, the respiration is increased and along with it a slight increase in sucrose content occurs. This inability of galactose, maltose and glycerin to increase the sucrose content recalls the observations made by Meyer[7] who found leaves of several kinds of plants were able to form starch when floated on aqueous solutions of sucrose, glucose or fructose, but only in one or two instances did he observe any starch formation when the leaves were floated on galactose, or glycerin solutions. Similarly, Parkin[8] found in the case of narcissus and iris leaves that maltose, in contrast to sucrose, glucose and fructose, gave rise to only very little starch formation.

Another factor involved in the formation of sucrose noticed in the case of potato slices, which has not been mentioned by Waterman, or de Wolff, nor by Schroeder and Horn or Ahrns, in the case of leaves, is the effect of oxygen or air. When potato slices are dried in an atmosphere of nitrogen, no increase, or at least very little, in sucrose content occurs, and the same is true when the slices, dipped in a glucose solution, are stored wet in an atmosphere of nitrogen. This necessity of oxygen for the formation of sucrose seems to be like the dependence on oxygen noticed in the transformation of starch into sucrose in the ripening of fruit. Thus Bailey[9] found when green bananas were coated with paraffin or immersed in oil so

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(6) E. F. Hopkins, *Bot. Gaz.*, 84, 75 (1927).

(7) A. Meyer, *Bot. Z.*, 44, 104, 128 (1886).

(8) J. Parkin, *Trans. Roy. Soc., London*, 191B, 35 (1899).

(9) E. M. Bailey, This Journal, 34, 1706 (1912).

as to keep the fruit from being in contact with air, the decrease in starch as well as the increase in sucrose ceased. Miss Hemperly in this Laboratory (unpublished) since then has observed the same, and Thornton[10] finds that storing green bananas in an atmosphere of carbon dioxide prevents the starch from changing into sugar. The fact that oxygen is essential for changing reducing sugars in potato slices to sucrose shows that the reactions involved must be related in some way to aerobic respiration.

Experimental Procedure

1. **Variety of Potatoes Used.**—Mostly Irish Cobbler and Idaho Russets, all in the dormant condition.

2. **Slices.**—Tubers of fairly regular shape, about 10–15 cm. long and 5–7 cm. in diameter, were peeled and slices varying in thickness from 1 to 2 mm. cut from the middle portion of the tuber. Six slices weighing from 12 to 20 g. usually constituted an experimental sample.

3. **Slow Drying of Slices.**—Instead of drying the slices by warming them to about 30 to 40° over a low gas flame as was done by Waterman and de Wolff, the slices were usually dried at room temperature in a desiccator by means of anhydrous calcium chloride. For this purpose, the slices were distributed on a large perforated porcelain disk which constituted the shelf in the large 10-inch desiccator. Supported above the porcelain disk by means of three or four corks was a large watch glass containing the calcium chloride. By choosing the right amount of the drying agent it was possible to lower the weight of the sample from 15 to 75% in ten to twenty hours.

TABLE I

Treatment	Orig. wt. of sample, g.	After storage, g.	Change in wt. during storage, %	Time of storage, hrs.	Orig. non-reducing sugar content, %[a]	Non-reducing sugar content after storage, %	Increase in non-reducing sugar, %
Idaho Russet Potatoes							
20% Glucose[b]	25.035	26.226	+ 4.0	18	0.16	0.83	420
20% Fructose[b]	22.227	23.440	+ 5.0	22	.13	.90	590
20% Galactose[b]	25.310	26.750	+ 5.0	18	.16	.25	56
20% Maltose[b]	20.476	20.660	+ 0.9	21	.15	.35	133
20% Glycerin[b]	14.640	13.040	−10.0	22	.12	.07	− 42
20% Distilled water[c]	13.677	14.031	+ 2.6	19	.26	.43	65
Irish Cobbler Potatoes Bought in the Open Market							
Untreated[d]	23.754	22.805	− 4.0	24	.19	.39	100
20% Glucose + N_2[e]	16.438	14.434	−12.0	19	.15	.29	93
Air and $CaCl_2$[f]	21.360	4.705	−78.0	19	.10	.52	400
N_2 and $CaCl_2$[g]	23.627	9.363	−60.0	22	.10	.11	10

[a] The content of non-reducing sugar, hydrolyzed by invertase, contained in the freshly cut slices. [b] Slices dipped in 20% sugar solutions, then stored in desiccator containing air saturated with water vapor. [c] Slices dipped in distilled water and then stored in desiccator containing air saturated with water vapor. [d] Slices not dipped in any solution, just stored in desiccator containing air saturated with water vapor. [e] Slices dipped in 20% glucose and then stored in desiccator in an atmosphere of nitrogen. [f] Freshly cut slices stored in desiccator containing calcium chloride and dried slowly. [g] Freshly cut slices stored in desiccator containing calcium chloride and dried slowly in an atmosphere of nitrogen.

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(10) N. C. Thornton, "Contributions from Boyce Thompson Institute," 3, 219 (1931).

4. Storing the Slices.—In order to show that no desiccation is necessary for the sucrose formation when the slices have been dipped in an aqueous glucose or fructose solution, it was necessary to keep the slices moist while being exposed to air. Instead of the watch-glass containing calcium chloride suspended over the slices on the porcelain disk, the bottom of the desiccator was covered with a layer of water. This kept the air sufficiently saturated with water vapor so that the slices suffered no appreciable change in weight on remaining in the desiccator for several hours.

5. Dipping Slices in Hexose Solutions.—The freshly cut slices were placed in 20% hexose solution, allowed to remain in the latter for two to three minutes, removed and either dried and stored as described in 3 or stored wet as indicated in 4.

6. Determination of Sugars.—The slices, after they had been stored in the desiccator for the desired length of time, or, in the case of the control samples, immediately after they were cut, were placed in 75 cc. of 95% ethyl alcohol and boiled on the water-bath for ten minutes. The slices were then removed from the alcohol, ground to a powder in a mortar and the ground material and alcohol used for washing the mortar returned to the original alcohol. The latter was then diluted by the addition of 25 cc. of water, placed in a flask and agitated in a shaking machine for two hours and filtered. The filtrate containing the dissolved sugars together with the alcohol washings was then distilled under reduced pressure at about 45° to remove the alcohol, the aqueous residue clarified by lead acetate and the reducing sugars determined, before and after inversion by yeast invertase, by means of copper reduction.[11]

The following table is given to show the degree of precision in the determinations of the sucrose content. Six samples of potato slices were cut from the same potato, three for determining the sucrose content immediately after cutting the slices, and three for the sucrose content after dipping in 20% glucose solution and being stored for twenty-two hours in a desiccator containing moist air.

Experiment number	1	2	3
Non-reducing sugar in fresh slices	0.13	0.12	0.12
Non-reducing sugar after dipped in glucose solution and stored wet for 22 hrs.	1.15	1.11	1.09

Summary

1. Contrary to the conclusions of earlier investigators, it has been shown that dehydration of potato slices is not necessary in order to effect marked increases in sucrose content.

2. Evidence has been given that sucrose in the potato is synthesized from glucose or fructose, rather than, as has been supposed, in some more direct way from starch.

3. It has been shown that the presence of oxygen is necessary for the formation of sucrose in the potato slices.

New York City

Received May 17, 1933
Published September 5, 1933

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[11] Waterman, Ref. 4, isolated from the alcoholic extract of potato slices, dried at 35°, crystals of sucrose, m. p. 180°; 88 mg. dissolved in 20 cc. of water, gave a rotation in a 2-dcm. tube $[\alpha]_D$ +54° (calcd. +58°).

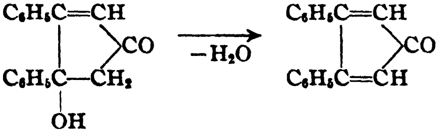
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

The Reactions of Anhydracetonebenzil. II[1]

BY C. F. H. ALLEN AND E. W. SPANAGEL

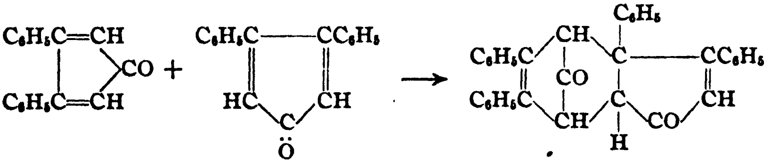
The most characteristic reaction of anhydracetonebenzil (I) is the ease with which it loses water and forms a "bimolecular product" when treated with acidic dehydrating agents. Japp[2] and Gray[3] observed that the homologs of (I) exhibited the same behavior, as long as there was one hydrogen left in the alpha position and adjacent to the hydroxyl group, but neither suggested a possible structure for the new type of substance. They also found that the latter lost quantitatively one molecule of carbon monoxide on pyrolysis, and that the resulting product formed a monophenylhydrazone. The problem has been investigated in this Laboratory and the results are described in this communication.

In a previous paper[4] it was suggested that a cyclopentadienone (II) was the primary product of dehydration, although it was never isolated.



I II

This substance contains two conjugated systems, one that of an α,β-unsaturated ketone and the other that of a diene, so should enter into a diene synthesis with itself. Assuming that it did so, it was possible to write the structure (III) for the bimolecular product; its correctness was then verified by a long series of reactions that ultimately gave *o*-diphenylbenzene.



III

This tricyclic ketone forms a dioxime; the carbonyl groups are not linked alike, one being removed readily as carbon monoxide on heating. *A priori*, it would be expected that the bridge would be more easily lost, leaving a bicyclic ketone (IV); the presence of a conjugated system in (IV) was shown by the addition of maleic anhydride to give (V)—the latter could be more conveniently prepared directly from the bimolecular product

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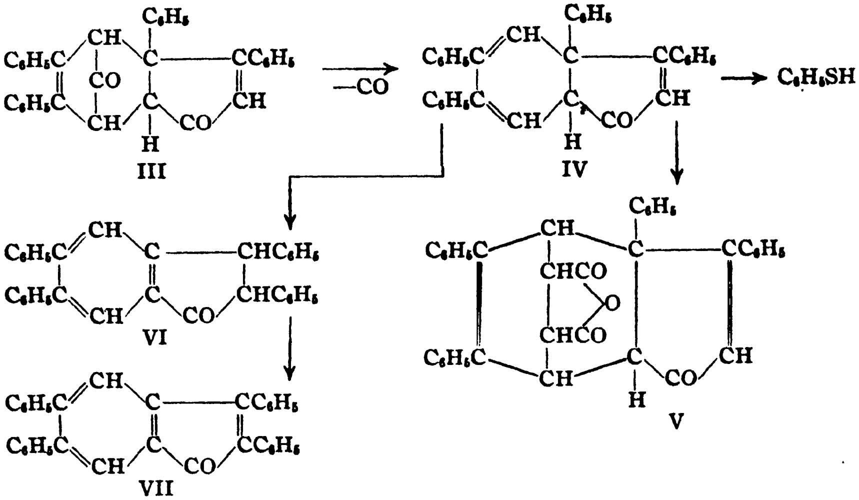
[1] This paper is a more extended presentation of results originally embodied in a Communication to the Editor received November 25, 1932.

[2] Japp and co-workers. This long list of references is given in detail in the previous paper.[4]

[3] Gray, *J. Chem. Soc.*, **95**, 2131 (1909).

[4] Allen and Spanagel, THIS JOURNAL, **54**, 4338 (1932).

(III), because the ketone (IV) very easily underwent a rearrangement on pyrolysis, resulting in the indanone (VI).

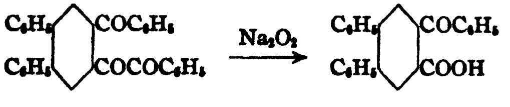


III IV V VI VII

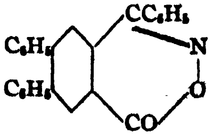
The bicyclic ketone (IV) is pale yellow, forms an oxime and yields thiophenol when heated with sulfur. The use of sulfur to detect alkyl radicals attached to carbon atoms common to two rings has been widely employed by Ruzicka[5] but this is the first instance of which we are aware when an aryl group has been so removed.

The indanone (VI) is colorless; it does not react with maleic anhydride but forms a monophenylhydrazone corresponding in physical properties with the one described by Japp, so that his pyrolysis product was probably (VI); this is to be expected since it is only by working cautiously that (IV) survives the heating necessary to remove the carbonyl bridge. It is easily dehydrogenated by sulfur to the deep red indone (VII); the color of the latter is deeper than that of diphenylindone.[6]

This red ketone forms an oxime and mono-*p*-bromophenylhydrazone, and is readily oxidized to a yellow triketone (VIII), but does not add maleic anhydride. The triketone is cleaved by sodium peroxide to benzoic acid and a ketonic acid (IX); when the preparation of an oxime of the latter was attempted, an indifferent compound containing nitrogen resulted—it was not affected by phosphorus pentachloride and had no active hydrogen, and probably is best represented as the orthoxazine (X).



VIII IX



X

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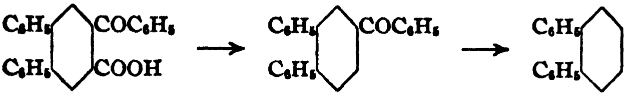
(5) Ruzicka, *Helv. Chim. Acta*, **5**, 349 (1922).

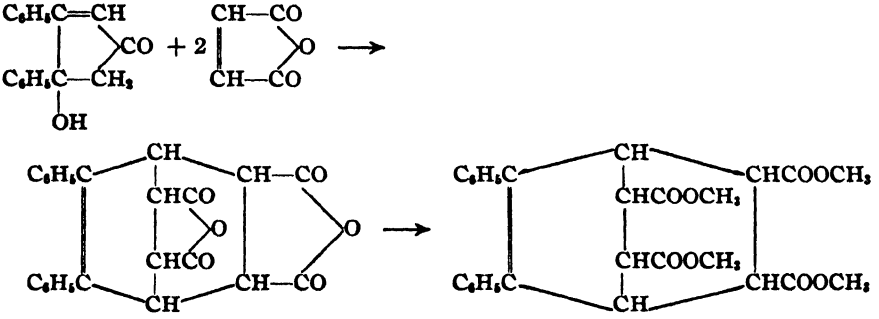
(6) Heyl and Meyer, *Ber.*, **28**, 2776 (1895).

On decarboxylation of the acid (IX) a diphenylbenzophenone was obtained in poor yield; it formed a monoxime which by the Beckmann rearrangement gave an uncrystallizable anilide. This was hydrolyzed to a glass-like amine which, when diazotized in alcoholic hydrochloric acid and warmed with copper powder, gave an oil from which *o*-diphenylbenzene was separated by vacuum distillation.



IX

The transient existence of the cyclopentadienone (II) can be shown by using an excess of maleic anhydride as a dehydrating agent for anhydracetonebenzil; on heating to about 200°, carbon monoxide and water are lost and a solid dianhydride (XI) is formed; the latter is readily converted into a tetramethyl ester. The reaction proceeds in steps, but the description of the intermediate products and their reactions, along with a similar series from tetraphenylcyclopentadienone, will form the subject of a later communication. It is sufficient here to note the similarity to Diels' reactions between coumalin and maleic anhydride.[7]

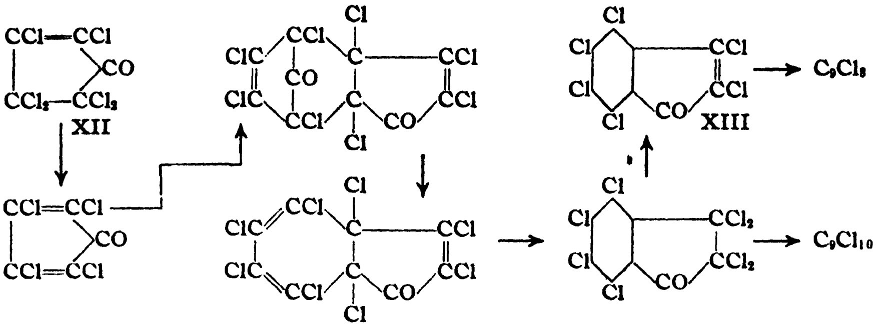


XI

After a clue had been obtained as to the structure of the bimolecular product, one analogous case was discovered in the literature; Zincke[8] prepared a highly chlorinated cyclopentenone (XII) and found that on reduction with stannous chloride a bimolecular product was obtained; when heated, the latter lost chlorine and carbon monoxide to form a perchlorindone (XIII); the carbonyl group was detected by chlorination with phosphorus pentachloride. He likewise assumed that a cyclopentadienone was the primary product and converted the indone into tetrachlorophthalic acid to show the presence of a benzene ring.

(7) Diels, Alder and Müller, *Ann.*, **490**, 257 (1931).

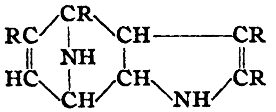
(8) Zincke and co-workers, *Ber.*, **21**, 2719 (1888); **22**, 486 (1889); **23**, 812 (1890); **26**, 2104 (1893); *Ann.*, **272**, 243 (1892); **296**, 135 (1897); **367**, 1 (1909); **394**, 7 (1912).

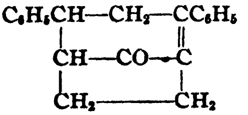


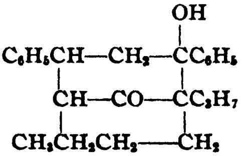
Since then the structure of dicyclopentadiene has been shown to be of a similar nature.[9]

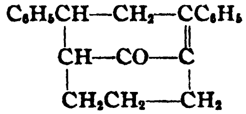
The above work suggests that the dipyrroles are similarly constituted and should be represented as in formula (XIV). The correctness of this assumption is being tested.

Very few other substances having a carbonyl bridge are known; Stobbe[10] has described two (XV, XVI) and a third (XVII) has been prepared in this Laboratory. None of them lose carbon monoxide when heated unless the molecule is entirely decomposed; from a study of mechanical models it was evident that in the latter type the CO bridge formed part of a strainless ring, whereas it was impossible to construct a model of the diketone (III) described in this paper without great distortion. A previous attempt to prepare an unsaturated bicyclic system having a carbonyl bridge was unsuccessful.[11]


XIV


XV


XVI


XVII

Experimental

A. Dehydrogenation of Anhydracetonebenzil; "the Bimolecular Compound"; 3a,4,7,7a-Tetrahydro-3,3a,5,6-tetraphenyl-4,7-methanoindene-1,8-dione (III).—An almost quantitative yield was obtained by warming a mixture of 60 g. of glacial acetic acid, 50 g. of finely powdered anhydracetonebenzil and 10 cc. of concd. sulfuric acid nearly to boiling with frequent shaking, until the deep red color had changed to a light brown (about ten minutes). The substance separated on cooling and was purified by crystallizing from a benzene–alcohol mixture. It formed two dioximes when treated with hydroxylamine acetate in the usual way. After two hours of heating one was isolated in the form of rods, readily soluble in alcohol, m. p. 176°; the isomer was the

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(9) Alder and Stein, *Ann.*, **485**, 211, 223 (1931).

(10) Stobbe, *J. prakt. Chem.*, **86**, 210 (1912).

(11) Allen, *Can. J. Res.*, **4**, 264 (1931).

principal product after twenty-four hours of heating—it is only slightly soluble in alcohol; m. p. 229°.

Anal. Calcd. for $C_{34}H_{26}O_2N_2$: N, 5.7. Found: (229°) N, 5.7; (176°) N, 5.1.

When acetic anhydride and sulfuric acid are used for the dehydration a small amount of an acetate can be isolated by careful manipulation; this is very soluble in the usual organic solvents; it separates from alcohol in clusters of prisms, m. p. 91°.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 77.9, 77.8; H, 5.3, 5.1

On hydrolysis with dilute ammonia the bimolecular compound resulted, but alcoholic potash gave a new substance that crystallized in thick prisms, m. p. 280°.

Anal. Found: C, 85.2, 84.8; H, 5.3, 6.2.

It does not react with acetyl chloride, or acetic anhydride and sulfuric acid; owing to the small amount available it was not further investigated.

B. Pyrolysis of (III); Preparation of the Isomers, 3a,7a-Dihydro-3,3a,5,6-tetraphenylinden-1-one (IV) and 2,3,5,6-Tetraphenylindan-1-one (VI).—In a small flask 25 g. of the bimolecular product was heated by a metal bath at 210° for ten minutes; carbon monoxide was evolved rapidly. The cooled melt was dissolved in benzene and alcohol added to precipitate 10 g. of the white indanone (V); the filtrate slowly deposited 10 g. of the yellow isomer. After purification the white substance melted at 176°, and the pale yellow isomer at 167°; mixed melting points showed a marked depression. The indanone (VI) is fairly soluble in acetone, acetic acid and benzene, but only slightly soluble in alcohol and ether; it crystallizes in characteristic five-sided plates. It did not decolorize permanganate or bromine instantly. It is undoubtedly the substance described by Japp, though he gave a range of melting points.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5. Found: C, 90.9; H, 5.5.

The oxime, prepared in the usual way, separated from alcohol in leaflets, m. p. 225°.

Anal. Calcd. for $C_{33}H_{25}ON$: N, 3.1. Found: N, 3.0.

It gave a phenylhydrazone of m. p. 250° as previously described.

C. The Yellow Ketone (IV).—It was difficult to secure this substance unless the temperature of the pyrolysis was very carefully controlled; on heating too long or at a higher temperature it rearranges to the indanone—this change even takes place slowly in boiling alcoholic solutions.

It is readily soluble in acetone, benzene and decalin but sparingly in alcohol and ether; it separates in yellow rods from alcohol, m. p. 167°.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5. Found: C, 90.7; H, 5.4.

The oxime, made by the customary procedure, crystallized from alcohol in fine yellow prisms, m. p. 130° (unsharp).

Anal. Calcd. for $C_{33}H_{25}ON$: N, 3.1. Found: N, 3.5.

It gave a phenylhydrazone, m. p. 250°, probably the same as the one from the indanone, since a mixed melting point showed no depression. This may be accounted for by the ease of rearrangement noted above, which takes place during the sealed tube treatment required to prepare the phenylhydrazone.

Anal. Calcd. for $C_{39}H_{30}N_2$: N, 5.3. Found: N, 5.4.

It added maleic anhydride to form the tetracyclic substance (V), but a large part was isomerized at the same time to the indanone; the new product was more conveniently prepared from the bimolecular compound. The indanone did not react with maleic anhydride.

3a,4,5,7,7a-Hexahydro-1-keto-3,3a,8,9-tetraphenyl-4,7-ethanoindene-5,6-dicarboxylic Anhydride (V).—A mixture of 5 g. of the bimolecular compound and an equal *weight of maleic anhydride was heated by an oil-bath at the boiling point as long as carbon monoxide was given off (fifteen minutes), cooled and 15 cc. of methyl alcohol* added to remove the excess anhydride; the 4 g. of solid that was insoluble was recrystallized from acetic anhydride, from which it separated in rods, m. p. 301°. It is slightly soluble in alcohol, but very soluble in acetic acid, acetic anhydride and acetone.

Anal. Calcd. for $C_{37}H_{26}O_4$: C, 83.1; H, 4.9; mol. wt., 534. Found: C, 83.3; H, 5.0; mol. wt., 549.

It dissolved readily in dilute sodium hydroxide, but the acid obtained by acidification turned into the anhydride so easily that no attempt was made to obtain it pure.

On heating 10 g. of (IV) with 1 g. of flowers of sulfur in a small distilling flask at 325°, under slight suction, for a half hour it became black, but 0.2 g. of thiophenol collected in the receiver; the latter was converted into the 2,4-dinitrophenyl thioether, m. p. 121°, by Bost's procedure;[12] a mixed melting point with an authentic specimen showed no depression, m. p. 121°. Nothing could be separated from the black residue; if the temperature was kept lower, only an odor of thiophenol was noticed, and the rearrangement product (the indanone) was found—this doubtless accounted for the low yield of thiophenol; the sulfur reaction requires a higher temperature than the isomerization.

D. The Indenone (VII).—The indanone was readily dehydrogenated by heating with sulfur to give the new red ketone; the latter was oxidized with scission of the five-membered ring to a 1,2-diketone (VIII) which was readily cleaved by sodium peroxide; the keto acid (IX) thus resulting gave an indifferent substance containing nitrogen when treated with hydroxylamine acetate—presumably the orthoxazine (X).

2,3,6,7-Tetraphenylinden-1-one (VII).—A mixture of 25 g. of the pure indanone and 1 g. of flowers of sulfur in a small distilling flask under slight suction was heated for a half hour at 325°; hydrogen sulfide was evolved and the mass became a deep red. When cold, ether was added, the unused sulfur filtered, and on addition of alcohol and partial evaporation 16 g. (65%) of the red ketone crystallized. It is readily soluble in ether, acetone, acetic acid and benzene, but only slightly soluble in the alcohols; it forms red rods, m. p. 166°.

Anal. Calcd. for $C_{33}H_{22}O$: C, 91.2; H, 6.1. Found: C, 91.1; H, 5.1.

The yield was not increased by varying the temperature, amount of sulfur or addition of copper sulfide. It could be made, without isolation of the intermediates, from pure bimolecular product, if the latter was first heated to 250° for some time before the addition of the sulfur. The oxime, prepared as usual, crystallized from chloroform in fine yellow needles, m. p. 292°.

Anal. Calcd. for $C_{33}H_{23}ON$: N, 3.1. Found: N, 3.2.

The *p*-bromophenylhydrazone was never obtained pure; a brownish product was separated from the reaction mixture and repeatedly crystallized from *n*-butyl alcohol until it had a constant melting point, 226°.

Anal. Calcd. for $C_{39}H_{27}N_2Br$: Br, 13.2. Found: Br, 11.4, 11.9, 13.7.

1,2-Diphenyl-4-benzoyl-5-phenylglyoxylbenzene (VIII).—To a suspension of 10 g. of finely powdered red ketone in 60 cc. of acetic acid was added 8 g. of chromic acid, and the mixture refluxed for ten minutes; on addition of 300 cc. of ice water a fine yellow solid separated. This was filtered, dried and recrystallized from benzene and alcohol, from which it separated in yellow rosets, m. p. 183°. The yield was 7.9 g. (78%). It is slightly soluble in alcohol and ether, but readily soluble in benzene, acetone and acetic acid.

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(12) Bost, Turner and Norton, This Journal, 54, 1985 (1932).

Anal. Calcd. for $C_{33}H_{22}O_3$: C, 85.0; H, 4.7. Found: C, 85.1, 85.1; H, 5.0, 4.7.

The same substance was obtained in a smaller yield by the use of permanganate in acetone. The quinoxaline was prepared nearly quantitatively in the usual manner; it is sparingly soluble in alcohol, but crystallizes well from that solvent in cubes, m. p. 184°.

Anal. Calcd. for $C_{39}H_{26}ON_2$: N, 5.2; mol. wt., 538. Found: N, 5.0; mol. wt., 540.

E. 2-Benzoyl-4,5-diphenylbenzoic Acid (IX); Cleavage of the Diketone.—A solution of 5 g. of sodium peroxide in 50 cc. of ice water was added slowly with vigorous shaking to a suspension of 10 g. of the finely powdered triketone in 100 cc. of alcohol; the yellow solid slowly dissolved and shiny flakes formed. After a half hour the mixture was poured into water (filtered if necessary) and acidified with acetic acid—the acid slowly separated, was filtered after five hours, and recrystallized from dilute methyl alcohol. It is very soluble in organic solvents and dilute alkaline solutions. The yield was 7.6 g. (90%); m. p. 250°.

Anal. Calcd. for $C_{26}H_{18}O_3$: C, 82.5; H, 4.8. Found: C, 82.0; H, 4.7.

The filtrate was steam distilled and the benzoic acid identified in the usual way. When 1 g. of the keto acid was refluxed with hydroxylamine acetate in alcohol, white needles separated almost quantitatively, after an hour; the new product is almost insoluble in alcohol, but very soluble in benzene and chloroform; it slowly dissolves in dilute potash after long boiling. It melts at 225°.

Anal. Calcd. for $C_{26}H_{17}O_2N$: N, 3.7. Found: N, 3.5, 3.4.

It was recovered unchanged after an attempted Beckmann rearrangement using phosphorus pentachloride in absolute ether for twenty-four hours.

F. The Keto Acid (IX) and its Degradation to *o*-Diphenylbenzene.—The yields in each step were very low from this point on.

3,4-Diphenylbenzophenone.—A mixture of 5 g. of the keto acid and 0.5 g. of copper carbonate was heated at 225° for twenty minutes in a small distilling flask and then distilled *in vacuo;* the pale yellow oil was taken up in acetone—after dilution with methyl alcohol white prisms slowly separated; the yield was 1.5 g. (34%), m. p. 133°. It is soluble in the common organic solvents except alcohol.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.8; H, 5.4. Found: C, 89.9; H, 5.5.

The oxime crystallized from dilute alcohol in fine, white needles, m. p. 156°; the yield was 50%.

Anal. Calcd. for $C_{25}H_{19}ON$: N, 4.0. Found: N, 4.3.

A mixture of 1 g. of the oxime, 1.5 g. of phosphorus pentachloride and 20 cc. of absolute ether was left for a day at room temperature, then poured into water, the ether layer separated, dried with sodium sulfate and the solvent allowed to evaporate; 1 g. of a viscous oil remained—it could not be purified so was hydrolyzed by refluxing with alcoholic potash; on dilution with water an oil precipitated and was extracted with ether—it gave a strong qualitative test for nitrogen. Since it showed no tendency to crystallize it was taken up in 5 cc. of alcohol, 6 cc. of 1:1 hydrochloric acid added, the mixture well cooled and 0.2 g. of sodium nitrite introduced; when 0.1 g. of copper powder was dropped in gas bubbles became visible, and after a short warming ether was added, the upper layer separated, dried over sodium sulfate and distilled *in vacuo.* The 0.2 g. of pale yellow oil that was obtained slowly crystallized on standing; it had a melting point of 56° and showed no depression when mixed with some authentic *o*-diphenylbenzene.

G. The Reaction of Anhydracetonebenzil with Excess Maleic Anhydride; 7,8-Diphenylbicyclo-(2,2,2)-7-octene-2,3,5,6-tetracarboxylic Acid Dianhydride (XI).—In order to show that diphenylcyclopentadienone (II) was capable of at least a transitory existence,[13] it was heated with maleic anhydride as a dehydrating agent, and a sufficiently large excess used to allow for addition to the diene linkage. Equal weights of the two substances were heated in an oil-bath at 170°; the melt appeared to boil vigorously and carbon monoxide was evolved rapidly and burned with a large blue flame. The temperature was gradually raised until at about 230° the melt suddenly solidified; it was cooled somewhat, *p*-cymene added and the suspension filtered. The excess anhydride was washed out with hot methyl alcohol and the crude product recrystallized from *p*-cymene or acetic anhydride. It formed white flakes, shrinking at 334°, becoming liquid at 346° and giving off a gas at 356°.

Anal. Calcd. for $C_{24}H_{16}O_6$: C, 72.0; H, 4.0. Found: C, 71.5; H, 4.0.

It is insoluble in the alcohols, ether, acetone and carbon tetrachloride, sparingly soluble in *p*-cymene, but very soluble in ethyl acetate and acetic anhydride. It dissolves in sodium hydroxide; on acidification an acid is precipitated in fine needles—the melting point is indefinite as it loses water and re-forms the anhydride.

The tetramethyl ester was prepared by saturating a mixture of 5 g. of the anhydride and 25 cc. of absolute methyl alcohol with hydrogen chloride; the solid dissolved and after a day a new solid separated in the form of white needles. It was recrystallized from absolute methyl alcohol, in which it is sparingly soluble; m. p. 188°.

Anal. Calcd. for $C_{28}H_{28}O_8$: OCH_3, 25.5. Found: OCH_3, 25.3.

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. The structure of the bimolecular product resulting from the dehydration of anhydracetonebenzil has been determined. It is a tricyclic ring system, containing a carbonyl bridge.

2. One carbonyl group is lost as carbon monoxide on heating. The resulting product contains a conjugated system and easily adds maleic anhydride; it also forms thiophenol when heated with sulfur, and rearranges to an isomeric indanone.

3. When heated with sulfur, the indanone loses hydrogen sulfide and forms a red indone; the latter was degraded to *o*-diphenylbenzene.

4. Anhydracetonebenzil and excess maleic anhydride give a complex polycyclic dianhydride.

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[13] Burton and Shopee [*J. Soc. Chem. Ind.*, 51, 981 (1932)] have criticized the mechanism suggested in the previous paper[8] for the formation of isomeric chlorides on the grounds that the possibility of an anionotropic change was disregarded, and cited as evidence the production of three isomeric dinitrophenylhydrazones for which they wrote three different structures. However, since Bredereck [*Ber.*, 65, 1833 (1932)] has recently shown (1) that stereoisomeric 2,4-dinitrophenylhydrazones are possible, (2) that they are differently colored and (3) that the yellow, less stable form is readily isomerized to the red, stable form, the above evidence is inconclusive, especially as they had both yellow and red hydrazones. Further, β,β-dimethylanhydracetonebenzil does not give an isomeric chloride under the same conditions as the parent substance—this point was tested carefully—so that in view of these facts, as well as the production of the various addition products described in this paper, the assumption of an intermediate cyclopentadienone seems justified.

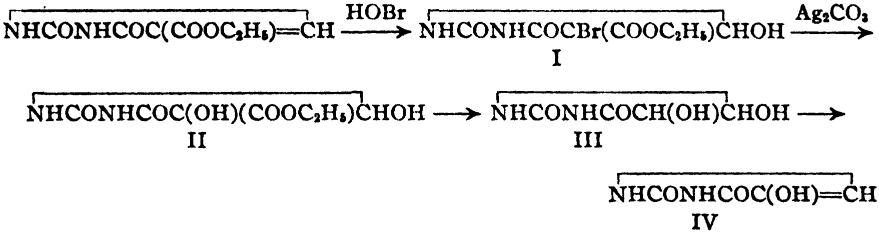
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Researches on Pyrimidines. CXXXV. Uracil-glycol

BY TREAT B. JOHNSON AND ELIZABETH DYER[1]

An investigation of methods for synthesizing uracil-glycol (5,6-dihydroxyhydrouracil) was undertaken in order to compare the properties of this pyrimidine with those of the corresponding thymine-glycol previously prepared in this Laboratory.[2]

The method used successfully by Baudisch and Davidson to prepare thymine-glycol is not directly applicable to uracil-glycol because of the non-existence of the necessary bromoxyuracil.[3] The 5-carbethoxy derivative of uracil glycol (II), however, was obtained in good yield by this method by starting with uracil-5-ethylcarboxylate and operating through the hydroxy-bromo ester represented by Formula I. The glycol II was obtained by the action of silver carbonate on this hydrogenated pyrimidine I.



$$\mathrm{NHCONHCOC(COOC_2H_5){=}CH} \xrightarrow{\mathrm{HOBr}} \underset{\mathrm{I}}{\mathrm{NHCONHCOCBr(COOC_2H_5)CHOH}} \xrightarrow{\mathrm{Ag_2CO_3}}$$

$$\underset{\mathrm{II}}{\mathrm{NHCONHCOC(OH)(COOC_2H_5)CHOH}} \longrightarrow \underset{\mathrm{III}}{\mathrm{NHCONHCOCH(OH)CHOH}} \longrightarrow \underset{\mathrm{IV}}{\mathrm{NHCONHCOC(OH){=}CH}}$$

The glycol ester (II) was expected to give uracil-glycol (III) upon saponification and decarboxylation. The product obtained, however, was not the desired glycol, but isobarbituric acid (IV). This pyrimidine was produced in all attempts at hydrolysis of the glycol ester (II), even under the mildest of experimental conditions. The intermediate 5-carboxylic acid could not be isolated, since it decomposed as soon as formed with the simultaneous elimination of carbon dioxide and water and the formation of isobarbituric acid. An acetyl derivative of the glycol ester (II) could be prepared, but it too gave only isobarbituric acid on hydrolysis.

The formation of isobarbituric acid instead of uracil-glycol was found to be a general reaction in other procedures designed to give the uracil-glycol. When isodialuric acid was reduced catalytically, isobarbituric acid was obtained. Even when the hydroxyl groups of isodialuric acid were protected through the use of the corresponding diacetate, the product formed was isobarbituric acid or its monoacetyl derivative.

The uracil-glycol configuration is thus seen to be too unstable for isolation. This is in marked contrast to the behavior of thymine-glycol, which may easily be prepared and purified,[3] and which forms an anhydride only on long standing in acid solution. It may, therefore, be concluded that loss of water takes place in uracil-glycol by withdrawal of the hydroxyl group in the 6-position with the free hydrogen atom in the 5-position of the pyrimidine ring. An analogous mobility of groups in the 6-position of 2,4-dioxypyrimidines has been demonstrated by Biltz.[4]

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[1] The Chemical Foundation, Incorporated, Research Fellow in Organic Chemistry.

[2] Baudisch and Davidson, *J. Biol. Chem.*, 64, 233 (1925); Johnson, Baudisch and Hoffmann, THIS JOURNAL, 54, 1106 (1932).

[3] Wheeler and Johnson, *J. Biol. Chem.*, 3, 187 (1907).

The tendency of derivatives of uracil-glycol to pass into isobarbituric acid is of interest in connection with the fact that the latter substance is known to be an oxidation product of uracil.[5] Evidence that isobarbituric acid may be an intermediate product in the metabolism of uracil *in vivo* as well as *in vitro* has been presented recently by Cerecedo.[6] It is conceivable that the unstable uracil-glycol may be the precursor of the isobarbituric acid in any metabolic processes involving oxidation.

Experimental Part

5-Carbethoxy-5-bromo-6-hydroxyhydrouracil (I).—Eight grams of powdered 5-carbethoxyuracil[7] was suspended in 70 cc. of water, 2.5 cc. of bromine (1.1 equivalent) was added, and the mixture was allowed to stand for twelve hours at ordinary temperature with occasional shaking. As the original ester dissolved, colorless crystals of the bromoxy ester were formed. The precipitate was filtered, washed with water, dissolved in 150 cc. of boiling water and the solution filtered hot. The pyrimidine crystallized from the cooled solution in the form of long, colorless needles, melting at 178° (corr.) with effervescence; yield 7.3 g. (59%).

Anal. Calcd. for $C_7H_9O_5N_2Br$: N, 9.96; Br, 28.47. Found: N, 9.90, 9.87; Br, 28.29, 28.12.

The ester was decomposed by heat or by acids with the loss of hypobromous acid. By action of silver carbonate it was transformed into the glycol ester (II).

5-Carbethoxy-5,6-dihydroxyhydrouracil (II).—Four grams of (I) and 2.2 g. of powdered silver carbonate (1.1 equivalent) were suspended in 150 cc. of water, and the mixture was stirred for ten hours at room temperature. After adding alcohol to prevent foaming, the precipitated silver bromide was filtered through a norit mat and the excess of silver then removed from the solution with hydrogen sulfide, and the clear colorless filtrate evaporated to dryness *in vacuo* at 40–50°. The crystalline residue was dissolved in a small quantity of dry acetone, filtered from traces of inorganic matter and the filtrate evaporated nearly to dryness. The pure glycol ester was then precipitated by adding ether to the concentrated acetone solution; yield 3.0 g. (97%).

The immediate product of the reaction was a hydrated form of the glycol ester which readily lost one mole of water of crystallization when heated *in vacuo* at 61°. The pure hydrated form, when heated in a melting point tube, softened at 72°, melted partially around 110°, with violent effervescence at 125°. The anhydrous modification melted sharply with effervescence at 135–136° (corr.). The glycol ester is insoluble in ether, but very soluble in alcohol, water and acetone, from which it crystallizes upon evaporation as colorless plates. It gives no blue color with ferric chloride, unlike isobarbituric acid.[8]

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(4) Biltz and Paetzold, *Ann.*, **452**, 71 (1927).

(5) Baudisch, *J. Biol. Chem.*, **60**, 155 (1924).

(6) Cerecedo, *ibid.*, **88**, 695 (1930).

(7) Wheeler, Johnson and Johns, *Am. Chem. J.*, **37**, 398 (1907).

(8) Biltz and Paetzold, *Ann.*, **452**, 87 (1927).

Anal. Hydrate: Calcd. for $C_7H_{10}O_6N_2.H_2O$: H_2O, 7.63. Found: H_2O, 7.94. Anhydrous form: Calcd. for $C_7H_{10}O_6N_2$: C, 38.53; H, 4.59; N, 12.84. Found: C, 38.53, 38.10; H, 4.85, 4.61; N, 12.87, 12.79.

Hydrolysis of II.—When a dilute hydrochloric acid solution of the glycol ester II was warmed, carbon dioxide was evolved immediately, and a granular precipitate separated, which was identical in properties and analysis with an authentic specimen of isobarbituric acid.[8] When the glycol ester was saponified with one equivalent of potassium hydroxide in cold absolute alcohol solution, a white amorphous potassium salt was obtained. By careful acidification of this salt in cold aqueous solution, isobarbituric acid was the only product obtained.

Monoacetate of 5-Carbethoxy-5,6-dihydroxyhydrouracil.—A mixture of 1 g. of the glycol ester and 8 cc. of acetic anhydride was boiled for three minutes. The resulting solution was concentrated in a vacuum desiccator until the monoacetate crystallized; yield 0.4 g. (33%). This substance was moderately soluble in cold acetone, from which it crystallized as clusters of colorless needles, melting at 178° (corr.) with effervescence.

Anal. Calcd. for $C_9H_{12}O_7N_2$: C, 41.52; H, 4.65; N, 10.77. Found: C, 41.86; H, 4.84; N, 10.95.

Study of Other Methods Applied for Synthesizing Uracil-glycol

(1) **Bromination of 5-Carboxyluracil.**—Attempts to add one equivalent of hypobromous acid to 5-carboxyluracil[9] suspended in water resulted in the partial decarboxylation of the acid, even in the cold, with the formation of 5,5′-dibromo-6-hydroxyhydrouracil. The product was identical in properties and analysis with a synthetic specimen.[3] The remainder consisted solely of unchanged 5-carboxyluracil. By using two equivalents of bromine water, a 90% yield of the dibromohydroxyhydrouracil was obtained.

(2) **Reduction of Isodialuric Acid and Diacetyl-isodialuric Acid.**—Upon reduction of 4 g. of pure isodialuric acid[10] in ethanol solution with the Adams platinum catalyst,[11] 0.3 g. of isobarbituric acid was isolated together with 3.4 g. of unchanged isodialuric acid. When 2.4 g. of diacetylisodialuric acid[12] was hydrogenated in glacial acetic acid solution, 0.7 g. of isobarbituric acid was obtained. Similarly, when the solvent was a mixture of acetic acid and acetic anhydride, acetyl isobarbituric acid[12] was formed in 66% yield.

(3) **Oxidation of Uracil with Peracetic Acid.**—Uracil was not attacked by treatment with 90% peracetic acid[13] for long periods at 25°, 40° or at 80° under pressure. Experiments were carried out both with and without solvents (water and acetic acid).

(4) **Reduction of Isouramil.**—Attempts to obtain dihydroisouramil by catalytic reduction of isouramil[14] in aqueous ammonia solutions were unsuccessful.

Summary

Free uracil-glycol could not be isolated because of its great tendency to pass into isobarbituric acid with loss of water. The lability of this pyrimidine glycol is in marked contrast to the comparative stability of the corresponding 5-methyl derivative (thymine-glycol) and the 5-carbethoxy derivative described in this paper.

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(9) Wheeler, Johnson and Johns, *Am. Chem. J.*, **37**, 399 (1907).

(10) Behrend and Roosen, *Ann.*, **251**, 242 (1889).

(11) "Organic Syntheses," 1928, Vol. VIII, p. 92.

(12) Biltz and Paetzold, *Ann.*, **452**, 88, 89 (1927).

(13) Arbusow, *J. prakt. Chem.*, **131**, 365 (1931).

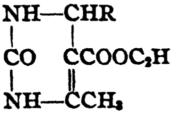
(14) Bogert and Davidson, *Proc. Nat. Acad. Sci.*, **18**, 495 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Researches on Pyrimidines. CXXXVI. The Mechanism of Formation of Tetrahydropyrimidines by the Biginelli Reaction[1]

BY KARL FOLKERS[2] AND TREAT B. JOHNSON

The reaction of numerous aldehydes with urea and a β-keto ester to give a tetrahydropyrimidine was discovered by Biginelli.[3] Structure I, as formulated by Biginelli, may be used to represent these tetrahydropyrimidines, in which R is the grouping joined to —CHO of the particular aryl, alkyl or arylalkyl aldehyde employed in conjunction with urea and ethyl acetoacetate. Accordingly, when benzaldehyde was used, Biginelli obtained a pyrimidine which he considered to be represented by structure II, namely, 2-keto-4-phenyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine, and he studied this member of his series in greatest detail. In their short study of this reaction, Biginelli's structure II was apparently accepted by Hinkel and Hey;[4] and in a recent extended study[5] of the condensation, no contradictory constitutional evidence was found.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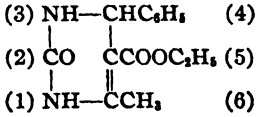
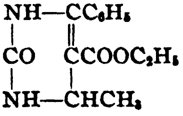

II


III

Since a conception of mechanism which was based on experiments designed for the purpose was greatly needed, the authors have studied further the formation of pyrimidine II in an effort to obtain mechanism formations which would be of value in their further application of the condensation. The data obtained and their interpretations are summarized in this paper. As a basis, the Biginelli pyrimidine formula, II, was accepted. Evidence in favor of it with regard to the position of the double bond was the preparation of the isomeric pyrimidine, III, and the hydrogenation of pyrimidine III[6] and pyrimidine II[7] to the same 4-cyclohexylhexahydropyrimidine derivative, and then the saponification of this reduced ester to the 5-pyrimidine carboxylic acid. Very recently, Bergmann and Johnson[8] have confirmed the pyrimidine structure, I, by a new and different synthesis of 2-keto-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine of which these pyrimidines may be considered 4-substituted derivatives.

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(1) Presented, in part, at the Washington Meeting of the American Chemical Society, March, 1933.

(2) E. R. Squibb and Sons Research Fellow in Organic Chemistry.

(3) Biginelli, *Ber.*, **24**, 1317 (1891); *Gazz. chim. ital.*, **23**, 360 (1893).

(4) Hinkel and Hey, *Rec. trav. chim.*, **48**, 1280 (1929).

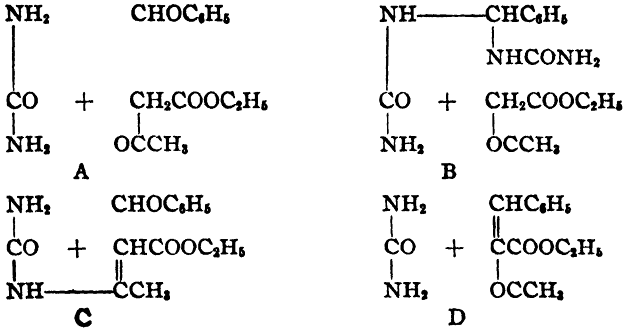
(5) Folkers, Harwood and Johnson, THIS JOURNAL, **54**, 3751 (1932).

(6) Folkers and Johnson, *ibid.*, **55**, 1140 (1933).

(7) Folkers and Johnson, *ibid.*, **55**, 2886 (1933).

(8) Results that are to be published soon from this Laboratory.

In his original work, Biginelli showed, as his constitutional proof, that pyrimidine II could be obtained experimentally in four different ways. The systems of reactants representing these four methods are: (A) urea, benzaldehyde and ethyl acetoacetate; (B) benzal-bisurea and ethyl acetoacetate; (C) ethyl β-carbamidocrotonate and benzaldehyde; and (D) urea and ethyl α-benzalacetoacetate. Systems B, C and D represented the three primary bimolecular reactions that were possible from system A.



A B C D

Since it seemed improbable that the three components of system A reacted simultaneously to give the pyrimidine, queries that followed were: which reactants (B, C or D) were formed from A and that lead to pyrimidine II and at what rate and to what extent? Which system by itself leads to the pyrimidine most readily and to the greatest extent? Are the true systems leading to the pyrimidine not system B, C or D, but precursors or derived products of them, etc.?

In conjunction with the reactants, the catalytic effects had also to be considered. It has been well demonstrated before, and by this paper, that this condensation proceeds exceedingly slowly, if at all, unless catalyzed by acid, and it has been indicated[6] that when the pyrimidine was

TABLE I[a]

EFFECT OF CATALYST ON THE RATE OF FORMATION OF PYRIMIDINE II

Catalyst	Amount	Percentage yield[c]
....	.....	(0.38)[b]
Iodine	<0.3 g.	33.1
Iodine	.3 g.	56.1
Sulfuric acid (concd.)	4 drops[d]	67.0
Hydrochloric acid (concd.)	2 drops	53.8
Hydrochloric acid (concd.)	4 drops	67.0
Hydrochloric acid (concd.)	8 drops	74.6

[a] Based on runs of 0.05 mole each of urea and benzaldehyde and 0.075 mole of ethyl acetoacetate dissolved in 20 ml. of abs. ethanol and refluxed for two hours. [b] Obtained by pouring solution into 300 ml. of water and allowing twenty-four hours for crystallization. [c] Yields represent the amount of pyrimidine separating from reacted solution. [d] 5-ml. pipet.

obtained without the use of a definite catalyst, the derived acetic acid was the catalytic factor. Further data on the effect of catalysts on the formation of pyrimidine II are given in Table I. The reacted solution with iodine as catalyst was distinctly acid to litmus, so the acid formed was probably the prime catalytic agent. Quite evidently, within limits, the yield was proportional to the amount of catalyst present. When ten drops of piperidine were used as catalyst, there was no formation of pyrimidine II, but benzaldehyde and the ethyl acetoacetate reacted to give a 39.8% yield of the β_1-form of 1-methyl-2,4-dicarbethoxy-3-phenyl-5-keto-cyclohexanol.[9] Although the chief interests of Table II were the comparative system yields of the pyrimidine, it clearly demonstrated, again for system A and anew for systems B and C, that the yield was proportional to the amount within limits of the catalyst present.

The reaction between citral, urea and ethyl acetoacetate gave two pyrimidines, one of m. p. 150–150.8° and the other of m. p. 109.5–110.5°.[5] On hydrogenation with a platinum catalyst, these isomers each absorbed very easily 2 moles of hydrogen to give the same product, namely, 2-keto-4-(2,5-dimethyl-heptyl)-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine. Therefore, the citral employed contained at least two of the known citral isomers, probably the diastereoisomers, each of which gave a pyrimidine, and since the isomerism was in the side chain and not the pyrimidine nucleus, further study of the isomers was irrelevant.

Experimental

There are given in Table II the yields of pyrimidine II as obtained with varying amounts of catalyst by the four systems of reactants under comparable conditions. These same data are presented in part in the curves of Fig. 1 for better visualization and discussion. The quantities of reactants for the systems were: (A) 0.025 mole each of urea, redistilled benzaldehyde and acid-free ethyl acetoacetate; (AA) 0.05 mole of urea and 0.025 mole each of benzaldehyde and ethyl acetoacetate; (B) 0.025 mole each of benzal-bisurea[10] and ethyl acetoacetate; (C) 0.025 mole each of ethyl β-carbamidocrotonate[11] and benzaldehyde; (D) 0.025 mole each of urea and ethyl α-benzalacetoacetate.[12]

The reactants in each run were dissolved in 35 ml. of absolute ethanol. This amount of solvent was not sufficient in all runs to keep the mixture homogeneous. However, it was not desirable to increase the amount of solvent, even to overcome this criticism. Concentrated sulfuric acid was used as the catalyst because of its low volatility and its low water content. It did not seem necessary to try to eliminate the last traces of water from the initial solution because of the water formed in the actual condensation. Each run was refluxed for two hours and then allowed to stand at 25° for twelve to fifteen hours for crystallization. This period of reaction was arbitrary and affixed so that data on the reaction rates would be obtained. Therefore, the yields as secured with the lower

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(9) M. p. 151–152° (corr.). Hantzsch gave m. p. 152–153° [*Ber.*, **18**, 2583 (1885)].

(10) Schiff, *Ann.*, **151**, 192 (1869).

(11) Behrend, *Ann.*, **229**, 5 (1885); Donleavy, unpublished results of this Laboratory. The crude product obtained for the preparation of 6-methyl-uracil was recrystallized from dilute ethanol.

(12) Knoevenagel, *Ber.*, **29**, 172 (1896); **31**, 730; Claisen and Matthews, *ibid.*, **218**, 178 (1883).

TABLE II

COMPARATIVE YIELDS OF PYRIMIDINE II FROM THE SYSTEMS

Catalyst, concd. sulfuric acid, drops	Percentage yields from systems A	AA	B	C	D[d]
0	0[a]	..	..	0[a]	..
1	13.9	21.5	..	40.0	0
2	29.2	..	46.1	47.7	..
3	40.0	50.8	54.6	53.8	0
3	55.4[b]	..	..	..	..
6	53.8	..	71.5	..	..
12	66.1	70.7	76.1	69.2	0[c]
16	..	..	..	64.6	..
20	66.1	73.8	79.2	66.1	0
30	..	..	78.4	..	..
35	..	..	..	..	0
50	..	..	..	..	0

[a] On pouring the reacted solution into 300 ml. of water and allowing to stand for twenty-four hours, there were no crystals of the pyrimidine present. This testified to the scarcity of water in the absolute ethanol and the lack of free acid in the ethyl acetoacetate. [b] Solution refluxed for seven hours instead of two hours. [c] The yield was also zero when four drops of water were added. [d] Yields of 1.5–3.8% of pure pyrimidine were obtained by pouring the solution into 300 ml. of water, etc.

concentrations of catalyst are those from interrupted reactions. The yields of Table II represent that amount of pyrimidine crystallizing out of the original solution. Actually these are the minimum yields, for there is a small amount remaining in solution. However, the systems are best compared on these yields. The solubility of pyrimidine II in 95% ethanol at 25° is about 0.35 g. per 35 ml. In each case the filtrate and the 5 ml. of wash alcohol were poured into 300 ml. of water to precipitate the last of the pyrimidine with a small amount of gummy material. After fifteen hours this solid was filtered and dried. The percentage of pyrimidine in this material decreased as the amount of catalyst for the run was increased, and varied in quantity as follows: (A) 0.6–1.2 g.; (AA) 0.5–0.9 g.; (B) 0.5–0.9 g.; (C) 0.9–1.0 g.; and for (D) the amount was only 0.1–0.25 g. of very pure pyrimidine. For accuracy, the benzaldehyde and ethyl acetoacetate were measured out from burets, and the ethyl α-benzalacetoacetate was measured from a calibrated tube. The urea was weighed to the hundredths and the benzal-bisurea and ethyl β-carbamidocrotonate to the tenths. The absolute ethanol was measured from pipets, and the drops of sulfuric acid were counted from a full 5-ml. pipet.

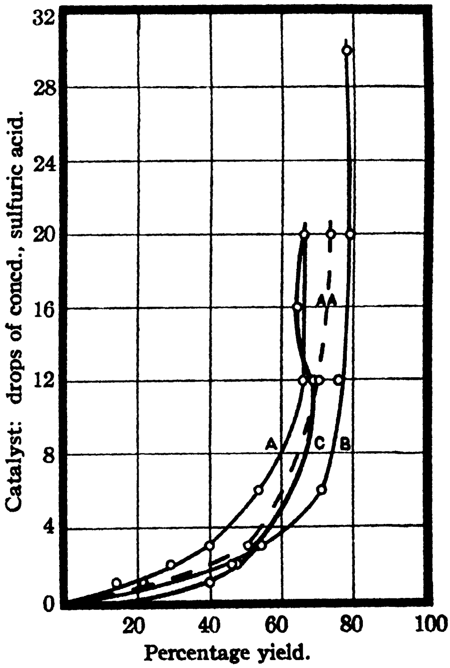

Fig. 1.—Comparative yields and rate of formation of pyrimidine II from the systems.

2-Keto-4-(2,5-dimethylheptyl)-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine.—Three and eight-tenths grams each of the pyrimidine of m. p. 109.5–110.5° and m. p. 150–150.8° (obtained by the interaction of citral, urea and ethyl acetoacetate) were reduced separately by dissolving in 80 ml. of glacial acetic acid and shaking under three atmospheres hydrogen pressure for four minutes in the presence of 0.2 g. of platinum catalyst. Each pyrimidine absorbed two moles of hydrogen. The solutions were concentrated under diminished pressure and the residues poured into 100 ml. of water. The oils quickly solidified, and, after two crystallizations from aqueous ethanol, melted (and mixed m. p.) at 131–134°.

Anal. Calcd. for $C_{17}H_{30}N_2O_3$: C, 65.75; H, 9.74. Found: (micro) C, 65.68; H, 9.71.

Discussion of Results

System A.—When only one or two drops of acid were used in the reaction between the three components, there was observed at the starting of refluxing a few white particles, probably benzal-bisurea,[13] which soon disappeared. The formation of this compound was the only indication of mechanism obtained from the three component system.

System B.—The reaction between benzal-bisurea and ethyl acetoacetate in the higher acid concentrations gave the highest yields of pyrimidine of any system. In this system there was a second molecular quantity of urea which was initially present in benzal-bisurea. Probably this second urea molecule functioned on the product side of the reaction. Benzal-bisurea was quite insoluble in hot absolute ethanol, and it was not appreciably affected when an alcohol suspension containing acid was refluxed. However, when ethyl acetoacetate was added to the solution, the insoluble benzal-bisurea disappeared and the pyrimidine precipitated, with a velocity proportional to the amount of acid used. If benzal-bisurea had broken down in some manner to give urea and benzaldehyde, then the increased yields of system B might have been due partially or wholly to a mass effect of this excess urea, for it was known that the yield was increased by the mass effect of excess ethyl acetoacetate. System AA was identical with A except for the use of a second molecular quantity of urea, and the increase in yield of system AA with respect to A was a measure of this mass effect. Since this increase in yield was only a part of the increase of B over A, it was concluded that system B constituted a definite step in the mechanism.

System C.—The yields of pyrimidine from the interaction of ethyl β-carbamidocrotonate and benzaldehyde were much greater than those of system A for low concentration of acid, but were almost identical for the higher concentrations of acid. This observation suggested that the mechanism of pyrimidine formation was the same for systems A and C for the higher concentrations of acid. Such a suggestion implied that at these higher concentrations of acid the ethyl β-carbamidocrotonate underwent hydrolysis into urea and ethyl acetoacetate, or, in other words, system C changed into system A. Evidence for such hydrolysis of ethyl β-carbamidocrotonate was found in the two following facts.

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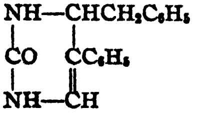
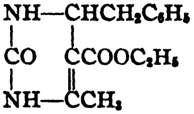
(13) Hinkel and Hey expressed their belief that the first action in this condensation consisted in the formation of benzal-bisurea.

First, it was recently discovered[14] that phenylacetaldehyde would react with urea under the same experimental conditions used for the preparation of pyrimidine II to form a new type of pyrimidine derivative, namely, 2-keto-4-benzyl-5-phenyl-1,2,3,4-tetrahydropyrimidine, IV. When phenylacetaldehyde reacted with ethyl β-carbamidocrotonate in the same quality absolute ethanol and under the high concentration of acid used for system C, pyrimidine IV was isolated again in good yield. The urea needed for this condensation could come only by the primary hydrolysis of the ethyl β-carbamidocrotonate.



$$\begin{array}{l} \mathrm{NH-CHCH_2C_6H_5} \\ \;|\qquad| \\ \mathrm{CO\quad CC_6H_5} \\ \;|\qquad\| \\ \mathrm{NH-CH} \end{array}$$

IV



$$\begin{array}{l} \mathrm{NH-CHCH_2C_6H_5} \\ \;|\qquad| \\ \mathrm{CO\quad CCOOC_2H_5} \\ \;|\qquad\| \\ \mathrm{NH-CCH_3} \end{array}$$

V

Second, when 0.025 mole each of benzal-bisurea and ethyl β-carbamidocrotonate reacted for two hours in 35 ml. of ethanol with 20 drops of catalyst, there was obtained an 81.5% yield of pyrimidine II. The formation of pyrimidine II, by system B in this case, showed the presence of ethyl acetoacetate which could come only by the hydrolysis of ethyl β-carbamidocrotonate.

Even though such a small quantity of water was present, probably the hydrolysis of ethyl β-carbamidocrotonate differed, with respect to the reactant and medium, only in degree from the reported hydrolysis of ethyl β-aminocrotonate into the ammonium salt and ethyl acetoacetate by an acidic solution at 25°.[15] The nitrogen–carbon bond of the $-\mathrm{N}-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-$ group in certain cyclic ureides is known also to be weak in acid solution.

Strong evidence that ethyl β-carbamidocrotonate did react directly with benzaldehyde is found in the much higher yields of pyrimidine II from system C in contrast with A for the low concentration of acid, and the fact that in the above-mentioned reaction between ethyl β-carbamidocrotonate and phenylacetaldehyde there also was isolated the 4-benzylpyrimidine derivative, V.

System D.—It was obvious from the exceedingly small yields of pyrimidine obtained by the interaction of urea and ethyl α-benzalacetoacetate that this system did not function directly in the three component process. This small yield of pyrimidine would require further study before statements regarding its formation would be warranted.

Mechanism Formulations.—From these results it appeared quite definite that pyrimidine II could be formed by the direct interaction of benzal-bisurea and ethyl acetoacetate (system B), and ethyl β-carbamidocrotonate and benzaldehyde (system C), and that these two systems were possibly related according to the following scheme:

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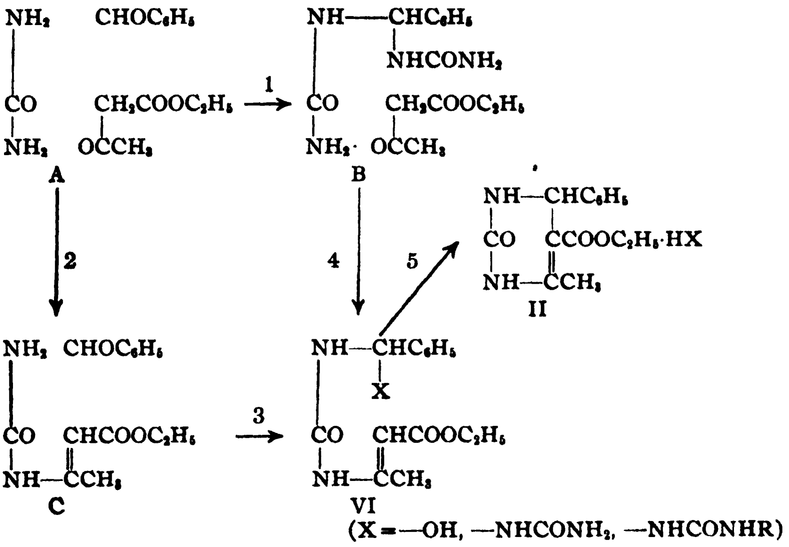
(14) Folkers and Johnson, THIS JOURNAL, **55**, 3361 (1933).

(15) Collie, *J. Chem. Soc.*, **71**, 303 (1898).



System B, or C, or both, might have first formed from system A. Then either, or both, of these systems, on reacting with the proper remaining component (ethyl acetoacetate for B and benzaldehyde for C) and then undergoing cyclization, formed pyrimidine II. The catalyzed mechanism of any individual step is as yet problematical. For this reason it was desirable to substitute "X" for the radical functioning in structure VI. The extent to which any of these steps proceeded or predominated would be expected to depend upon those factors which influence the relative rates of competitive reactions. There was support for this hypothesis. Step 4, or the formation of the 1,6-linkage, was a union well known in the chemistry of acyclic and cyclic ureides for its ease of formation. The experimental conditions for the preparation of benzal-bisurea indicated the ease of formation of the 3,4-linkage (step 3). Step 5 appeared as the slowest, or the rate-determining, step. Curve B (representing system B) of Fig. 1 is a measure of the combined rates of steps 4 and 5 and curve C of the combined rates of steps 3 and 5; and since steps 4 and 3 are conceived to be fast as compared with 5, then both curves should be an actual measure of step 5. This relationship was borne out by the near quality of yields for 1 to 3 drops of catalyst, as shown by curves B and C. The divergence of curve C for greater amounts of catalyst may be accounted for by the hydrolysis of the ethyl β-carbamidocrotonate. Steps 3 and 5 are somewhat related to the discussion of the condensation of secondary amines with aldehydes and naphthols.[16]

Biginelli and the present authors were unable to isolate a pyrimidine from the system ethyl α-ethylacetoacetate, urea and benzaldehyde. This hypothesis would explain such a failure, for the structure VII would have no hydrogen atom available for cyclization.

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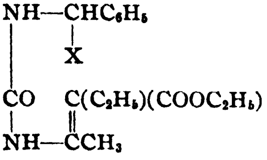
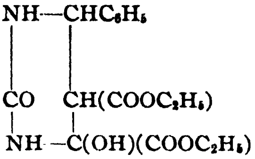
[16] Littman and Brode, This Journal, 52, 1655 (1930).


VII


VIII

By the interaction of ethyl oxalacetate, benzaldehyde and urea, Biginelli obtained the 6-hydroxypyrimidine, VIII, and from this, by dehydration, the tetrahydropyrimidine derivative. This would indicate for step 4 of the hypothesis the addition of the urea molecule to that of the β-keto ester (probably the keto form), followed by dehydration. That the hydroxyl group of the structure $-\mathrm{NHCONH\underset{|}{C}(OH)(CO_2C_2H_5)}$ is stabilized by the negative $-COOC_2H_5$ group is not unexpected. For example, ethylidene urea[17] results from the interaction of acetaldehyde and urea, but if chloral and urea interact, the intermediate product, β-trichloro-α-hydroxyethylurea, $Cl_3CCHOHNHCONH_2$, is isolated in good yields[18] and can then be converted to trichloroethylideneurea.

Summary

From a detailed study of the mechanism of formation of 2-keto-4-phenyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine from urea, benzaldehyde and ethyl acetoacetate by the Biginelli reaction, it has been concluded that the urea reacted first with benzaldehyde to form benzal-bisurea, or with the ethyl acetoacetate to form ethyl β-carbamidocrotonate. Then, one, or both, of these intermediates further reacted with the proper remaining component (ethyl acetoacetate and benzaldehyde, respectively), and by a final cyclization reaction the pyrimidine was formed. Evidence to support this formulation has been given. Direct interaction between urea and ethyl α-benzalacetoacetate did not appear to function directly in this mechanism.

It has been shown that ethyl β-carbamidocrotonate hydrolyzed with ease into urea and ethyl acetoacetate under the experimental conditions used in this study.

The two previously reported pyrimidine isomers, obtained by the condensation of citral, urea and ethyl acetoacetate, have been shown to have the cause of the isomerism in the heptadienyl side chain, and not the pyrimidine nucleus.

NEW HAVEN, CONNECTICUT

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[17] Schiff, *Ann.*, **151**, 204 (1869).

[18] Coppen and Titherly, *J. Chem. Soc.*, **105**, 32 (1914).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Trialkylethinylcarbinols

BY D. D. COFFMAN, JUNE CHIEN-YU TSAO, L. E. SCHNIEPP AND C. S. MARVEL

In some recent work[1] it has been shown that carbinols containing the group $—CH_2—C{\equiv}C—\overset{R}{\underset{R}{C}}—OH$ behave abnormally when treated with reagents which should yield the corresponding halide. Only two out of the five carbinols previously studied gave the expected halides and even in those cases the halogen compounds were too unstable to be isolated and had to be characterized by conversion to stable derivatives. The further work on compounds of this type has emphasized the peculiar reactions of acetylenic carbinols which have a primary alkyl group adjacent to the carbon atom carrying the triple bond.

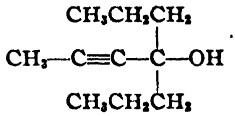
Three new acetylenic carbinols, namely, tripropinylcarbinol (I), trinonadecinylcarbinol (II) and di-*n*-propylpropinylcarbinol (III), have been selected for this study because they exemplify, respectively, the lowest molecular weight compound of this series, a very high molecular weight compound of this series and a compound in which the R group is a primary alkyl group.

$(CH_3—C{\equiv}C)_3COH$

I

$(CH_3(CH_2)_{16}—C{\equiv}C)_3COH$

II



$CH_3—C{\equiv}C—\overset{CH_3CH_2CH_2}{\underset{CH_3CH_2CH_2}{C}}—OH$

III

None of these carbinols which have primary alkyl groups attached to the acetylenic group behaved normally when treated with phosphorus trichloride. Neither trinonadecinylcarbinol nor di-*n*-propylpropinylcarbinol would yield a methyl ether on treatment with methyl alcohol and sulfuric acid.[2]

A most unusual reaction was observed when trinonadecinylcarbinol was warmed with sulfuric acid in acetic acid. The simple Meyer and Schuster[3] rearrangement to yield the unsaturated ketone did not occur. Analysis and molecular weight determinations on the product obtained showed that in this reaction two molecules of the carbinol had combined and apparently the acetylenic bonds had been hydrated. The reaction has been formulated as

$$2(CH_3(CH_2)_{16}C{\equiv}C)_3COH \xrightarrow{+\ H_2O} (CH_3(CH_2)_{16}COCH_2)_3—C—O—C(CH_2CO(CH_2)_{16}CH_3)_3$$

However, the carbinol groups may be in the α-position with respect to the ether linkage. This unusual reaction did not occur when either tri-

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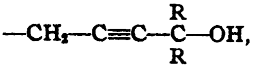
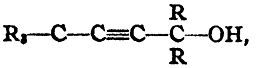
(1) Ozanne and Marvel, THIS JOURNAL, 52, 5267 (1930).

(2) Moureu, Dufraisse and Blatt, *Bull. soc. chim.*, [4] 35, 1412 (1924).

(3) Meyer and Schuster, *Ber.*, 55, 819 (1922).

propinylcarbinol or di-*n*-propylpropinylcarbinol was treated in a similar manner.

The reactions of the tertiary acetylenic carbinols of the type  $-CH_2-C\equiv C-\overset{R}{\underset{R}{C}}-OH$, which are reported in this communication, are quite different from the normal reactions of acetylenic carbinols of the type  $R_3-C-C\equiv C-\overset{R}{\underset{R}{C}}-OH$, which have been described previously.[4] Moreover, they are different from the reactions which Liang[5] has reported for secondary acetylenic carbinols of a related type.

Experimental

Bromo-2-nonadecene-1.—A solution of cetylmagnesium bromide in ether was prepared from 60 g. of cetyl bromide (b. p. 156–160° (1 mm.); m. p. 11.5°; n_D^{20} 1.4625) and 4.7 g. of magnesium in 300 cc. of dry ether according to the standard procedure. The reaction was started by adding a little cetylmagnesium bromide prepared from activated copper–magnesium alloy. The warm solution of cetylmagnesium bromide was filtered under nitrogen and then added to a well-cooled solution of 60 g. of dibromo-2,3-propene-1 in 100 cc. of anhydrous ether. The reaction mixture was then heated under a reflux condenser for about eighteen hours. During all of these operations a nitrogen atmosphere was maintained to avoid excessive oxidation of the Grignard reagent. After working up the reaction mixture in the usual way,[6] the bromo-2-nonadecene-1 was purified by fractional distillation under reduced pressure. The yield was about 10 g. (14.8% of the theoretical amount).

The residues from the fractional distillation were recrystallized from ether and gave some dotriakontane, m. p. 68–70°. If care was not taken to avoid oxidation of the Grignard reagent cetyl alcohol was present in the final mixture of products and could not be separated entirely from the bromo-2-nonadecene-1.

Bromo-2-nonadecene-1 is a colorless liquid; m. p. 10–10.5°; b. p. 168–172° (0.5 mm.); d_4^{20} 0.9781; n_D^{20} 1.4670; M_D, calcd. 97.24; found, 97.86.

Anal.[7] Calcd. for $C_{19}H_{37}Br$: Br. 23.19. Found: Br, 23.29.

Nonadecine-1.—The acetylene derivative was prepared from the bromo compound by the action of sodamide in xylene suspension.[6] A solution of 79 g. of the bromide in 50 cc. of xylene was added to a suspension of 30 g. of sodamide in 350 cc. of boiling xylene. After twelve hours the suspension was cooled, diluted with 1 liter of ether and worked up in the usual manner. On distillation under reduced pressure 40 g. (73% of the theoretical amount) of nonadecine-1 was obtained; b. p. 144° (1.5 mm.); m. p. 37–38°.

Anal. Calcd. for $C_{19}H_{36}$: C, 86.27; H, 13.73. Found: C, 86.51; H, 13.67.

Dinonadecinyl mercury was prepared by the method of Johnson and McEwen.[8] After recrystallization from *n*-butyl alcohol the product melted at 96–97°.

Anal. Calcd. for $C_{38}H_{70}Hg$: Hg, 27.59. Found: Hg, 27.76.

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[4] Salzberg and Marvel, THIS JOURNAL, 50, 1737, 2840 (1928); Rossander and Marvel, *ibid.*, 51, 932 (1929); Gillespie and Marvel, *ibid.*, 52, 3368 (1930); Davis and Marvel, *ibid.*, 53, 3840 (1931); Sweet and Marvel, *ibid.*, 54, 1184 (1932).

[5] Liang, *Bull. soc. chim.*, [4] 53, 33, 41 (1933).

[6] Lespieau and Bourguel, "Organic Syntheses," Coll. Vol. I, 1932, pp. 180, 185.

[7] This analysis was made by Mr. G. A. Jones.

[8] Johnson and McEwen, THIS JOURNAL, 48, 469 (1926).

Trinonadecinylcarbinol.—This carbinol was prepared from nonadecinylmagnesium bromide and diethyl carbonate[4] in yields of 43% of the theoretical amount. The product was purified by repeated recrystallization from absolute alcohol–ether mixtures; m. p. 71–72°.

Anal. Calcd. for $C_{58}H_{106}O$: C, 85.00; H, 13.05; mol. wt., 819. Found: C, 84.82; H, 12.97; mol. wt., 895.

The carbinol liberated the theoretical amount of ethane from a solution of ethylmagnesium bromide.

Methyl Trinonadecinylmethyl Ether.—To a solution of trinonadecinylcarbinol in benzene was added an ether solution of ethylmagnesium bromide. When the theoretical amount of ethane had been liberated, four times the calculated amount of dimethyl sulfate was added and the mixture was allowed to stand for about two days. The solvent was removed and absolute alcohol was added. On cooling the methyl trinonadecinylmethyl ether separated. After recrystallization from absolute alcohol, the product melted at 44–45°. The yield was better than 90% of the theoretical amount.

Anal. Calcd. for $C_{59}H_{108}O$: C, 85.00; H, 13.07. Found: C, 84.85; H, 12.94.

This ether could not be cleaved to yield a metallic alkyl by sodium–potassium alloy in ether solution. After this treatment the original ether was recovered.

Action of Sulfuric Acid on Trinonadecinylcarbinol.—When 1 g. of trinonadecinylcarbinol dissolved in 30 cc. of either ethyl alcohol or acetic acid was treated with 10 cc. of concentrated sulfuric acid and the solution was boiled for about one-half hour, a blue color developed. On dilution of the reaction mixture with water 0.6 g. of a blue compound was obtained by filtration. After recrystallization from ethyl acetate this product melted at 56–58°. An ether solution of this compound was blue in color but when this solution was treated with aqueous alkali the color changed to light brown. The blue color was regenerated on shaking the ether solution with dilute sulfuric acid. The blue compound did not contain sulfur.

Anal. Calcd. for $C_{116}H_{222}O_7$: C, 80.56; H, 12.95; mol. wt., 1728. Found: C, 80.61, 80.65; H, 12.50, 12.40; mol. wt., 1688, 1705.

Attempts to Prepare Trinonadecinylmethyl Bromide and Chloride.—When 2 g. of the carbinol was treated with 2 g. of acetyl bromide in ether or benzene at about 35° or when a solution of 5 g. of the carbinol in 5 cc. of ether was refluxed for forty-eight hours with 5 cc. of 40% aqueous hydrobromic acid, there was obtained a light yellow bromine-containing compound which melted at 37–38° after recrystallization from a mixture of benzene and alcohol. The bromine in this compound could not be removed with molecular silver but was removed completely by the action of 40% sodium amalgam or liquid sodium–potassium alloy. No metallic alkyl was produced by this latter treatment. The analysis and molecular weight indicate that the substance is not the expected bromide. No satisfactory explanation of the reaction involved here can yet be given.

Anal. Calcd. for $C_{58}H_{105}Br$: C, 78.93; H, 12.00; Br, 9.06; mol. wt., 882. Found: C, 74.33, 74.33, 74.8; H, 11.43, 11.23, 11.51; Br, 13.68, 13.68; mol. wt., 1132, 1167.

The carbinol in ether solution was treated with thionyl chloride and pyridine. There was thus obtained a chloro compound, m. p. 40–42°, which was also anomalous.

Anal. Calcd. for $C_{58}H_{105}Cl$: C, 89.74; H, 12.64. Found: C, 78.57; H, 11.71.

Tripropinylcarbinol.—Propine was prepared by heating 1390 g. of propylene bromide in a solution of 1750 g. of potassium hydroxide in 2 liters of *n*-butyl alcohol. The gaseous hydrocarbon was passed through two large U-tubes containing anhydrous calcium chloride and phosphorus pentoxide in order to remove alcohol and any possible moisture. The purified propine was passed into a solution of three moles of ethylmagnesium bromide in ether. This operation required about thirty-six hours. Unless this large excess of propine was used, ethylmagnesium bromide remained in the solution and produced mixtures of products.

To this solution of propinylmagnesium bromide was added 118 g. of diethyl carbonate over a period of about ten hours and the reaction carried out as usual for the preparation of acetylenic carbinols.[4] On final evaporation of the ether the carbinol remained as a dark colored solid weighing about 100 g. After repeated crystallization from hot benzene–petroleum ether (1–100) mixtures about 60 g. (41% of the theoretical amount) of yellow crystals (m. p. 134–135°) was obtained. Usually it was necessary to use decolorizing charcoal on the hot benzene solution to remove the deep color. The petroleum ether was then added and the crystals were obtained by cooling to 0° for several hours.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.15; H, 6.90; mol. wt., 146. Found: C, 82.58, 81.98; H, 7.07, 6.86; mol. wt., 141, 144, 145.

The structure of the carbinol was established by catalytic reduction to tri-*n*-propylcarbinol. A solution of 8 g. of the acetylenic carbinol in 150 cc. of 95% alcohol in the presence of 0.1 g. of platinum oxide catalyst[9] was reduced by hydrogen in about one hour. On working up the solution about 3 cc. of tri-*n*-propylcarbinol was isolated. This product had the following constants: b. p. 89–90.5° (21 mm.); d_0^{20} 0.8304; n_D^{20} 1.4337. A known sample of tri-*n*-propylcarbinol was found to have the following properties; b. p. 90–93° (21 mm.); d_0^{21} 0.8338;[10] n_D^{20} 1.43557.[10] No solid derivatives could be prepared for comparison.

Action of Phosphorus Trichloride on Tripropinylcarbinol.—A solution of 3 g. of the carbinol in 30 cc. of dry benzene was treated with 1 g. of phosphorus trichloride in 10 cc. of the same solvent under the conditions previously used for the conversion of acetylenic carbinols to the corresponding halides.[2,11] The product obtained after recrystallization from a mixture of alcohol and ether weighed 2 g. It was a yellow crystalline compound melting at 153–154° with violent decomposition. Analysis showed that the chlorine content was that expected but molecular weight determinations showed that the compound was a dimer.

Anal. Calcd. for $C_{10}H_9Cl$: Cl, 21.06; mol. wt., 164.5. Found: Cl, 21.03; mol. wt., 319, 324.

The chlorine in the dimer was not removed by shaking with molecular silver at ordinary temperature during three days. Sodium amalgam (40%) removed the halogen but did not form a metallic alkyl.

Some evidence was obtained that the monomeric chloride was formed and could be dehalogenated by silver if the reactions were all carried out at temperatures below −10°. However, it was impossible to obtain a hydrocarbon of sufficient stability to characterize.

Di-*n*-propylpropinylcarbinol.—The propine prepared from 606 g. of propylene bromide was passed into a solution containing 0.75 mole of ethylmagnesium bromide. Then 80 g. of di-*n*-propyl ketone was added and the reaction carried out in the usual fashion.[4] The carbinol boiled at 196–197° at atmospheric pressure. The yield was 64 g. (59% of the theoretical amount); d_{20}^{20} 0.8709; n_D^{20} 1.4518.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.92; H, 11.77. Found: C, 77.02, 77.49; H, 11.61, 11.58.

Catalytic reduction[9] of this carbinol gave tri-*n*-propylcarbinol; d_{20}^{20} 0.8340; n_D^{20} 1.4357.

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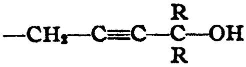
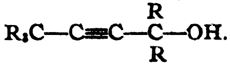
[9] Adams, Voorhees and Shriner, "Organic Syntheses," 1932, Coll. Vol. I, p. 452.

[10] Konowaloff, *Chem. Zentr.*, I, 1271 (1902).

[11] Moureu, Dufraisse and Mackall, *Bull. soc. chim.*, [4] 33, 934 (1923).

Treatment of the carbinol with phosphorus trichloride or tribromide gave liquid products which decomposed on distillation and were too low melting to crystallize. The same difficulty was met when thionyl chloride was used in place of phosphorus trichloride.

Summary

Three new acetylenic carbinols, tripropinylcarbinol, trinonadecinylcarbinol and di-*n*-propylpropinylcarbinol, which contain the group  $-CH_2-C\equiv C-\overset{R}{\underset{R}{C}}-OH$ have been characterized. Their behavior toward various reagents shows that they do not react in the manner which would be predicted from the knowledge gained previously from the study of closely related acetylenic carbinols containing the group  $R_3C-C\equiv C-\overset{R}{\underset{R}{C}}-OH$.

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[CONTRIBUTION NO. 43 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

The Direct Carboxylation of Carbon Compounds. II

BY CORLISS R. KINNEY AND OWEN W. WARD

In a recent study of the equilibrium $C_6H_5CO_2H \rightleftarrows C_6H_6 + CO_2$ it was found that benzene was carboxylated directly by carbon dioxide.[1] Temperatures of about 300° and pressures of about 30 atmospheres were used and the catalyst was of the Zn–Cu–Cr oxide type. Since the yield of acid product as well as the rate of the reaction was quite low, we have continued the search for a more active catalyst. In addition we have studied the direct carboxylation of a variety of compounds.

The experiments were all conducted in glass bomb tubes having a volume of 160 to 200 cc. Pressures of 20 to 30 atmospheres were obtained by introducing into each tube before sealing 0.1 mole of solid carbon dioxide. The tubes were heated for eight hours in a Carius furnace at the temperatures recorded in the table for each specific substance.

A catalyst was found to be quite essential for the carboxylation under the conditions given. The catalyst mentioned in the first paper was replaced by a similar mixture of oxides, but supported on asbestos. This change increased the activity of the catalyst based on the weight of metal oxides in the mixture. It was made by mixing thoroughly the well washed moist hydroxides obtained from 99 g. of $Zn(NO_3)_2 \cdot 6H_2O$ and 93.5 g. of $Cu(NO_3)_2 \cdot 3H_2O$ by precipitation with ammonium hydroxide, with 7.7 g. of chromic oxide and 40 g. of asbestos. After drying the mixture was ignited to convert the hydroxides to oxides. This type of catalyst was found to decrease in activity with use. Upon using the same catalyst over

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(1) Kinney and Langlois, THIS JOURNAL, 53, 2189 (1931).

for a second and a third time the yield of acid from toluene dropped from 0.36 to 0.15% and to 0.05% for the third run.

In attempting to avoid some of these difficulties a Ni–Co oxide catalyst was developed that was of approximately equal activity. It was made by dissolving 20 g. of $Ni(NO_3)_2 \cdot 6H_2O$ and 24 g. of $Co(NO_3)_2 \cdot 6H_2O$ in a small amount of water and mixing the solution with 15 g. of dry asbestos fiber. After drying the asbestos was ignited until no more oxides of nitrogen were evolved, when the catalyst was ready for use. This catalyst induced a yield of 0.33% of crude acid product from toluene as compared with 0.36% using the Zn–Cu–Cr oxide catalyst, consequently the latter catalyst was used in all the experiments recorded in the table.

After heating the various substances with carbon dioxide, two methods were used to isolate the products of carboxylation depending upon whether the substance was phenolic or not. In case the substance was not phenolic the contents of the tube were extracted with hot half normal potassium hydroxide. The acids were liberated with dilute sulfuric acid and extracted from the solution with several small portions of ether. The ether extract was dried with anhydrous sodium sulfate, filtered and the ether evaporated. The residue of crude acid was then treated as described below.

The reaction products from the phenolic compounds were extracted with a 10% sodium bicarbonate solution that had just been saturated with carbon dioxide. Since carboxylic acids displace carbonic acid from its salts while phenols do not it was possible to extract the phenolic compounds from the bicarbonate solution by repeated ether extractions. After making at least five such extractions with ether the bicarbonate solution was boiled with activated carbon and acidified with dilute sulfuric acid. The liberated acids were next extracted by several portions of ether, and isolated as described for the product from the non-phenolic substances above.

The crude acid products from toluene, anisole, nitrobenzene and styrene were purified by sublimation. In all other cases, the melting points and mixed melting points recorded in the table were obtained with the crude product.

The yields given in the table may not be the maximum obtainable since only two

TABLE

Substance used, g.	Temp., °C.	Calcd. press. in atm.	Yield of acid prod., %	M. p., °C.	Mixed m. p., °C.	M. p. of acid used for mixed m. p., °C.	Name of acid used for mixed m. p.
Toluene (2)	300–310		0.36	120–130	140–150	176	*p*-Toluic
Diphenylmethane (2) (a)	158–160	21.5	.19	140–143	143	146	Diphenylacetic
(b)	238–243	21.0	.44	141–142	143–144	146	
Triphenylmethane (2)	158–160	24.0	.33	259–260 dec.	260 dec.	263 dec.	Triphenylacetic
Styrene (3)	295–305	33.0	.28	120–121	129–129.5	133	Cinnamic
Phenol (2) (a)	115–117		Trace				
(b)	144–145	16.0	Trace				
(c)	205–208		None				
Anisole (2) (a)	218–222		Trace				
(b)	238–243	26.0	0.24	145–150	154–163	177	Anisic
Bromobenzene (6)	295–300	28.0	.14	220–222	238–239	251	*p*-Bromobenzoic
Dimethylaniline (3)	218–222	21.5	.10	209–210	213–214	230	*p*-Dimethylaminobenzoic
Nitrobenzene (3)	290–300	26.5	.21	220–222	230–230.5	237	*p*-Nitrobenzoic
Catechol (2) (a)	124–125	20.0	.64	117–124 dec.	135–148 dec.	197 dec.	2,3-Dihydroxybenzoic
(b)	170–173	19.0	Trace				
Resorcinol (1)	115–120	22.0	10.60	115–123 dec.	158–167 dec.	201 dec.	2,4-Dihydroxybenzoic
Quinol (2)	115–120	25.0	0.39	145–154 dec.	171–173 dec.	195 dec.	2,5-Dihydroxybenzoic

or three variations in temperature were made at most for any one substance. However the yields given were checked by duplicate runs. In addition, eight hours may be insufficient for the reaction to come to equilibrium as the rate of the reaction is probably low.

The melting point of the acid product in some cases was quite low compared to that of the pure acid used for comparison. For example the sublimed acid product from toluene melted 40–50° lower than the pure *p*-toluic acid used for the mixed melting point. The low melting point was probably due to the presence of a small amount of benzoic acid coming from the oxidation of the toluene by the oxide catalyst. This was verified by heating toluene with the catalyst in the absence of carbon dioxide, whereby a trace, compared to the yield of acid obtained when carbon dioxide was present, of a sublimable acid was obtained. If the impurity in the product from toluene was benzoic acid a study of mixed melting points showed that the sublimed acid contained only about 5% benzoic acid.

The products obtained from the dihydroxybenzenes were also very low melting. Again it appeared likely that the impurities were oxidation products as evidenced by their high color. In any event the impurity could not have been the unreacted phenolic compound as the method employed to separate artificial mixtures of the phenols and the corresponding carboxylated product was highly satisfactory. No explanation for the large yield from resorcinol can be offered at this time.

The carboxylation of diphenylmethane, triphenylmethane and styrene were of particular interest because of the carboxylation of aliphatic carbon-hydrogen bonds.

$$(C_6H_5)_2CH_2 + CO_2 \rightleftharpoons (C_6H_5)_2CHCOOH$$
$$(C_6H_5)_3CH + CO_2 \rightleftharpoons (C_6H_5)_3CCOOH$$
$$C_6H_5CH{=}CH_2 + CO_2 \rightleftharpoons C_6H_5CH{=}CHCOOH$$

The products of these three reactions were relatively pure and could be identified without trouble.

Likewise, bromobenzene, anisole, dimethylaniline and nitrobenzene gave fairly pure para carboxylation products considering the probability of simultaneous carboxylation in other positions.

In all cases studied thus far, with the possible exception of phenol, carboxylation has occurred. The reaction takes place with both aromatic and aliphatic carbon to hydrogen bonds; and, although the reaction is highly reversible with the position of equilibrium far on the side of decarboxylation, the reaction appears to be of a quite general nature.

SALT LAKE CITY, UTAH

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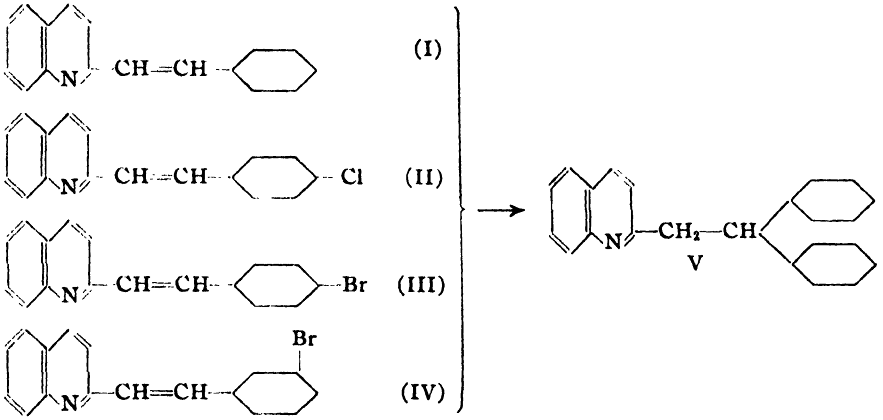
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reversible Addition of Aromatic Compounds to Conjugated Systems

BY REYNOLD C. FUSON, A. P. KOZACIK AND J. T. EATON

In a study of ring-chain conjugation in the quinoline series[1] it has recently been shown that benzalquinaldine (I) reacts with benzene in the presence of aluminum chloride to give α-benzohydrylquinaldine (V). This condensation is analogous to the addition under similar conditions of aromatic hydrocarbons to α,β-unsaturated carbonyl compounds—a reaction which has been observed by a number of investigators.[2]



However, with p-chlorobenzalquinaldine the reaction appeared to take a different course, for the product was not the expected α-(p-chlorobenzohydryl)-quinaldine but the chlorine-free α-benzohydrylquinaldine (V). This anomalous result has been subsequently investigated and the results are being reported in the present paper.

An early suggestion was that the removal of the chlorine might be due to the action of aluminum chloride alone; experiment showed, however, that p-chlorobenzalquinaldine was unaffected by long contact with aluminum chloride.

That the nature of the halogen atom or its position on the benzene ring might have a bearing on the result was also considered. It was found, however, that both p-bromobenzalquinaldine (III) and its meta isomer (IV) reacted smoothly to give α-benzohydrylquinaldine (V).

It now became apparent that the reaction involved not merely the

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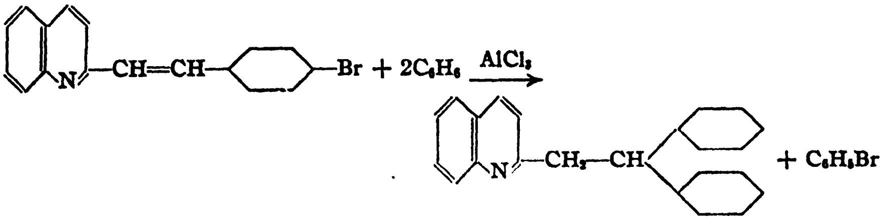
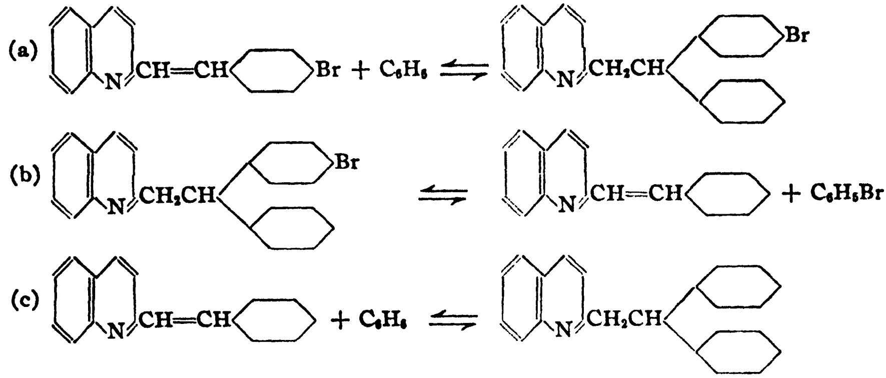
(1) Hoffman, Farlow and Fuson, THIS JOURNAL, **55**, 2000 (1933).

(2) (a) Eijkman, *Chem. Weekblad*, **4**, 727 (1907); **5**, 662 (1908); (b) Kohler, *Am. Chem. J.*, **42**, 375 (1909); Kohler, Heritage and Burnley, *ibid.*, **44**, 60 (1910); (c) Pummerer and Prell, *Ber.*, **55B**, 3105 (1922); Pummerer and Fiedler, *ibid.*, **60B**, 1439 (1927); Pummerer and Huppmann, *ibid.*, **60B**, 1445 (1927); (d) Vorländer and Friedberg, *Ber.*, **56B**, 1144 (1923); (e) Browning and Adams, THIS JOURNAL, **52**, 4098 (1930); Shildneck and Adams, *ibid.*, **53**, 343 (1931); (f) Rice, *ibid.*, **53**, 3153 (1931).

replacement of the halogen atom but that of the entire halophenyl radical. Experiments with *p*-bromobenzalquinaldine confirmed this deduction; it was found that *bromobenzene was produced in the reaction.* The reaction therefore is to be represented by the equation

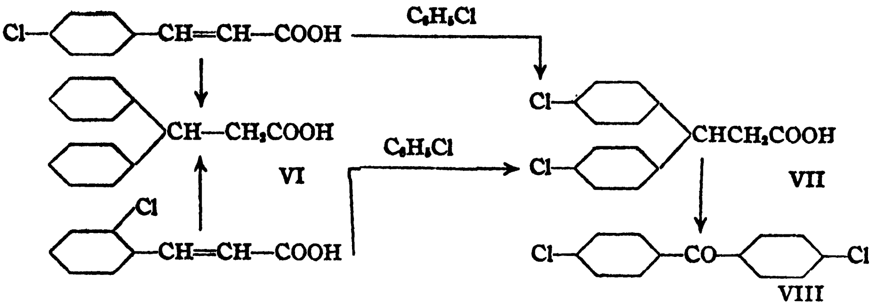


A possible explanation of these results is that the condensation is *reversible.* The reaction could then be resolved into the following three phases.



In a search for further evidence for the proposed mechanism it was found that the quinaldine derivatives were frequently difficult to handle, and efforts were made to determine whether the reaction was general for systems of the α,β-unsaturated carbonyl type. Nuclear halogen derivatives of cinnamic acid were found to behave in a manner entirely analogous to that observed with the halobenzalquinaldines and, consequently, subsequent studies have been carried out with the simpler system.

The Addition of Benzene and Chlorobenzene to *o*- and *p*-Chlorocinnamic Acids.—In the work with the chlorocinnamic acids it was first shown that both the *ortho* and the *para* chloro derivatives reacted with benzene in the presence of aluminum chloride to yield β,β-diphenylpropionic acid (VI). A crucial test of the theory was afforded by the addition of chlorobenzene to the two chlorocinnamic acids. It was found *that the addition products in the two cases were identical.* The product was β,β-di-(*p*-chlorophenyl)-propionic acid (VII). The positions of the chlorine atoms were established by degradation of the acid to the known *p,p'*-dichlorobenzophenone (VIII).



The mechanism suggested provides a satisfactory explanation of the result. Obviously, in the case of the *o*-chlorocinnamic acid the primary addition product is β-(*p*-chlorophenyl)-β-(*o*-chlorophenyl)-propionic acid, from which the *o*-chlorophenyl group is eliminated as chlorobenzene; the latter then condenses with the *p*-chlorocinnamic acid simultaneously produced. When chlorobenzene adds to the unsaturated acid, however, it reacts preferentially at the *para* position. It is evident that all of the facts obtained thus far are in agreement with the predictions based on the theory that the condensation is reversible.

Similar results have been obtained in work with α,β-unsaturated ketones. These will be reported separately but it may be said here that the later results furnish even more striking evidence in favor of the theory that the condensation takes place reversibly.

Experimental

***p*-Chlorobenzalquinaldine.**—The treatment of *p*-chlorobenzalquinaldine with aluminum chloride and benzene described in the preceding paper[1] was repeated except that the benzene was replaced by carbon disulfide and no hydrogen chloride was introduced. The yellow addition compound formed immediately but no further reaction took place; at the end of twelve hours the original base was recovered.

***m*-Bromobenzalquinaldine.**—This compound was prepared from *m*-bromobenzaldehyde and quinaldine by a procedure similar to that already described for the *p*-chlorobenzalquinaldine.[1] After recrystallization from alcohol the crystals melted at 96°.

Anal. Calcd. for $C_{17}H_{12}NBr$: Br, 25.8. Found: Br, 25.5.

The dibromide melted at 185–186°.

Anal. Calcd. for $C_{17}H_{12}NBr_3$: Br, 51.1. Found: Br, 51.3.

The action of benzene, aluminum chloride and hydrogen chloride on *m*-bromobenzalquinaldine was tested in the manner described for *p*-chlorobenzalquinaldine.[1] Here also the product was α-benzohydrylquinaldine.

***p*-Bromobenzalquinaldine.**—This base, prepared by the method already described for *p*-chlorobenzalquinaldine, melted at 137–138°.

Anal. Calcd. for $C_{17}H_{12}NBr$: Br, 25.8. Found: Br, 26.1.

The dibromide melted at 194–195°.

Anal. Calcd. for $C_{17}H_{12}NBr_3$: Br, 51.1. Found: Br, 51.3.

The action of benzene, aluminum chloride and hydrogen chloride on *p*-bromobenzalquinaldine gave α-benzohydrylquinaldine.

The excess benzene was washed with dilute acid, then with dilute carbonate solution and finally with water. The greater part of the benzene was distilled; the residue contained halogen and gave a refractive index (n^{20}_{D} 1.5145) somewhat higher than that of pure benzene (n^{20}_{D} 1.5010). Calculations based on the refractive index indicated that the residual liquid contained about 3 g. of bromobenzene, or 60% of the theoretical amount. This residual liquid (15 cc.) was placed in the usual Grignard apparatus and was treated with 0.5 g. of magnesium and 100 cc. of dry ether. When most of the magnesium had dissolved, 0.5 g. of phenyl isocyanate was added in small portions. There was a vigorous reaction. The mixture was heated under reflux for two hours after the addition was complete and then poured upon a mixture of 50 cc. of concentrated hydrochloric acid and 200 g. of ice. The solid which remained when the ether and benzene were evaporated was recrystallized from alcohol; colorless leaflets, melting at 160°. A mixture of these crystals with a sample of benzanilide also melted at 160°. The yield of benzanilide was 20% of the theoretical amount.

***p*-Chlorocinnamic Acid.**—This acid was prepared by the Perkin method, using potassium acetate in place of sodium acetate.[3] The yield was 66% of the theoretical amount; melting point, 246–247° (uncorr.).[4]

The action of benzene and aluminum chloride[5] on *p*-chlorocinnamic acid resulted in the formation of β,β-diphenylpropionic acid. To an ice-cold mixture of 20 g. of *p*-chlorocinnamic acid and 75 cc. of dry benzene was added 24 g. of pulverized anhydrous aluminum chloride. The flask containing the reaction mixture was kept in an ice-bath during the addition and was shaken frequently. When the evolution of hydrogen chloride had moderated the ice-bath was replaced by a water-bath maintained at a temperature of 35–40°. The shaking was continued and after an hour the mixture was decomposed by the addition of a mixture of 75 g. of ice, 75 g. of water and 24 g. of concentrated hydrochloric acid. The excess benzene was then removed by steam distillation and the product was extracted with ether. The solution was dried, the ether was distilled and the product was recrystallized from benzene. The β,β-diphenylpropionic acid melted at 153–154°. Eijkman[2a] gives the melting point as 154–155°.[6]

The action of chlorobenzene, aluminum chloride and hydrogen chloride was tested in the manner just described. In this case, however, the steam distillation was omitted and the product was separated from excess chlorobenzene by extraction with a solution of dilute alkali. The alkaline solution was then acidified and extracted with ether. Evaporation of the ether left the product as a viscous residue; recrystallization from alcohol gave crystals of β,β-di-(*p*-chlorophenyl)-propionic acid melting at 188–189°.

Anal. Calcd. for $C_{15}H_{12}O_2Cl_2$: Cl, 24.0. Found: Cl, 24.3.

***o*-Chlorocinnamic Acid.**—This acid was prepared by the method of Lasch,[3,7] yield, 73% of the theoretical amount.

The action of benzene and aluminum chloride was determined by use of the procedure already outlined for the preparation of β,β-diphenylpropionic acid from *p*-chlorocinnamic acid. The product was identical with that obtained in the experiment with the para isomer.

The action of chlorobenzene, aluminum chloride and hydrogen chloride, as in the case of *p*-chlorocinnamic acid, gave an acid which melts at 188–189° and which was shown by the mixed melting point method to be β,β-di-(*p*-chlorophenyl)-propionic acid.

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(3) This is an adaptation of the method used by Lasch [*Monatsh.*, **34**, 1653 (1913)] in the preparation of the ortho compound.

(4) Reich, Araus, Potok and Tempel [*Helv. Chim. Acta*, **3**, 793 (1920)], who made the acid by a similar procedure, give the melting point as 245°.

(5) In this case the introduction of hydrogen chloride was not necessary.

(6) See also Henderson, *J. Chem. Soc.*, **59**, 734 (1891).

(7) A similar method was used by Stoermer, *Ber.*, **44**, 637 (1911).

Oxidation.—A 1-g. sample of *β*,*β*-di-(*p*-chlorophenyl)-propionic acid was oxidized by heating it for six hours with a solution of 4 g. of potassium permanganate in 80 cc. of water. The alkali-insoluble product was crystallized from alcohol; melting point, 144–145°. This is the melting point given by Dittrich[8] for *p*,*p*'-dichlorobenzophenone.

Summary

It has been shown that in the presence of aluminum chloride and hydrogen chloride benzene adds to halobenzalquinaldines and to chlorocinnamic acids. In all of these cases the halophenyl group is replaced by an unsubstituted phenyl group, giving a benzohydryl derivative in place of the halobenzohydryl derivative which was to be expected.

In the case of *p*-bromobenzalquinaldine it has been shown that bromobenzene is a product of the reaction.

Chlorobenzene adds to *o*- and *p*-chlorocinnamic acids in the presence of aluminum chloride to give, in both instances, *β*,*β*-di-(*p*-chlorophenyl)-propionic acid.

It has been suggested that the condensation of aromatic compounds with *α*,*β*-unsaturated carbonyl compounds and similarly constituted systems is a reversible process. An interpretation of the results, based on this assumption, has been given.

(8) Dittrich, *Ann.*, **264**, 175 (1891). See also Norris and Green, *Am. Chem. J.*, **26**, 496 (1901).

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Preparation of Tetramethylmethane (Neopentane) and Determination of its Physical Constants[1]

BY FRANK C. WHITMORE AND GEO. H. FLEMING[2]

Tetramethylmethane has been prepared by relatively few workers and only its boiling point and freezing point have been reported. Because of the importance of the neopentyl system in rearrangements[3] the preparation and properties of the parent hydrocarbons have been studied.

This hydrocarbon has been obtained from petroleum,[4] also synthesized by the reaction of dimethylzinc with *tert*-butyl halides,[5] dimethyl sulfate with *tert*-butyl Grignard,[6] Grignards with halides,[7] and the hydrogenation of trimethylethylene in a silent electric discharge.[8] This formation is most interesting from the point of view of the current theory of rearrangements.[3]

(1) THIS JOURNAL, **54**, 3460 (1932).

(2) Presented in partial fulfilment of the requirements for the Ph.D. degree.

(3) Whitmore and co-workers, THIS JOURNAL, **54**, 3279, 3431 (1932); **55**, 1106, 1528 (1933).

(4) Markownikoff, *Ber.*, **32**, 1449 (1899); Poni, *Ann. Sci. Univ. Jassy*, **1**, 205 (1901).

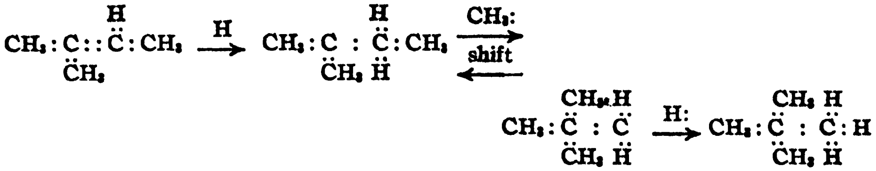
(5) Lwow, *Z. Chem.*, 520 (1870); dimethylzinc with 2,2-dichloropropane, *ibid.*, 257 (1871).

(6) Ferrario and Fagetti, *Gazz. chim. ital.*, **38**, [II], 630–634 (1908).

(7) Späth, *Monatsh.*, **34**, 1965–2014 (1913).

(8) Meneghini and Sargato, *Gazz. chim. ital.*, **62**, 621 (1932).

All the predictable products were obtained. The formation of neopentane may take place as follows



$$\mathrm{CH_3\!:\!\underset{CH_3}{C}\!::\!\overset{H}{\ddot{C}}\!:\!CH_3} \xrightarrow{\mathrm{H}} \mathrm{CH_3\!:\!\underset{CH_3}{C}\;:\;\overset{H}{\underset{H}{\ddot{C}}}\!:\!CH_3} \underset{\longleftarrow}{\xrightarrow[\text{shift}]{\mathrm{CH_3:}}}$$

$$\mathrm{CH_3\!:\!\overset{CH_3}{\underset{CH_3}{\ddot{C}}}\;:\;\overset{H}{\underset{H}{\ddot{C}}}} \xrightarrow{\mathrm{H:}} \mathrm{CH_3\!:\!\overset{CH_3}{\underset{CH_3}{\ddot{C}}}\;:\;\overset{H}{\underset{H}{\ddot{C}}}\!:\!H}$$

The fact that this involves the reverse of the ordinary rearrangement process[3] explains the small amount of neopentane found in the products. It is important to note that the fragment containing a carbon with only six electrons is formed by the *addition of a positive group* (H, in this case) instead of by the *removal of a negative group* with a complete octet of electrons.[3] This phenomenon is being intensively studied in this Laboratory.

Preparation of Neopentane

The work of Lwow was repeated using *tert*-butyl chloride and bromide as well as the iodide. The procedure consisted of adding a tetralin solution of the halide to the dimethylzinc, also in tetralin, at about 35°. The yields of neopentane were as follows: *tert*-butyl chloride, 51.2%; *tert*-butyl bromide, 46.1%; *tert*-butyl iodide, 42.0%.

Ferrario and Fagetti[6] report a 75% yield of neopentane by reaction of *tert*-butylmagnesium iodide with dimethyl sulfate in ether. This work was repeated using *tert*-butylmagnesium chloride in place of the iodide. A negligible quantity of neopentane was found. No improvement was obtained by using a higher boiling solvent (toluene).

E. Späth[7] treated methylmagnesium iodide with *tert*-butyl bromide but did not determine the yield of neopentane. This reaction was repeated and the yield found to be 18.2%. A toluene solution of the bromide was added to the Grignard reagent in ether and toluene at 40–49°.

The sodium salt of *tert*-butylacetic acid was fused with (1) soda-lime, (2) sodium hydroxide and (3) sodium methoxide, but in each case the yield of neopentane was negligible.

According to H. Fay[9] fatty acids are decomposed by uranyl nitrate in the presence of sunlight to give carbon dioxide and hydrocarbons. This reaction was tried with *tert*-butylacetic acid but even after two months' exposure only a very small quantity of gas was liberated.

Sabatier and Senderens,[10] and Mailhe[11] have found that fatty acids are decomposed by a nickel catalyst into carbon dioxide and hydrocarbons. When *tert*-butylacetic acid was decomposed in this manner at 350° it gave a 28.2% yield of neopentane. The apparatus used was of such design that the acid was distilled into a horizontal tube (30 × 1.2 cm.) containing 5.5 g. of freshly reduced nickel. By means of a reflux condenser the unchanged acid or other condensable material was returned to the flask. The gases formed by the decomposition were collected in gas-holders. It was found that starting with 10 g. of acid, only 4.1 g. was decomposed in thirteen hours.

The method finally adopted for the preparation of neopentane was the action of *tert*-butyl chloride and methylmagnesium chloride, both in toluene, at 45–50°. Consistent yields of 42–50% were obtained repeatedly.

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(9) Fay, *Am. Chem. J.*, 18, 269 (1896).

(10) Sabatier and Senderens, *Ann. chim. phys.*, [8] 4, 467 (1903).

(11) Mailhe, *Bull. soc. chim.*, [4] 5, 616 (1909).

Determination of Physical Constants of Neopentane.—The neopentane, free from olefins, was fractionated through a packed column (42 × 1.2 cm.) provided with total condenser and variable take-off.[12] The jacket of the column was maintained at 9–10° and the reflux condenser at 0–3°, by circulating suitably cooled water through them. The head of the column was heavily lagged with asbestos.

The distillate from the first fractionation, which consisted of 3.6 moles, was allowed to vaporize and after being scrubbed with 85% sulfuric acid, 25% potassium hydroxide, and dried with phosphorus pentoxide, was condensed. The middle cuts (2.6 moles) were combined and fractionated, the distillate being collected in four cuts. The freezing points of these cuts were found to be approximately −30, −25, −21 and −19°, respectively.

Refractive Index.—Refractive indices of the four cuts mentioned above were determined from 0 to +6° and the following values were obtained for cut 4 for n_D: 0°, 1.3513; 2°, 1.3498; 4°, 1.3486; 6°, 1.3476.

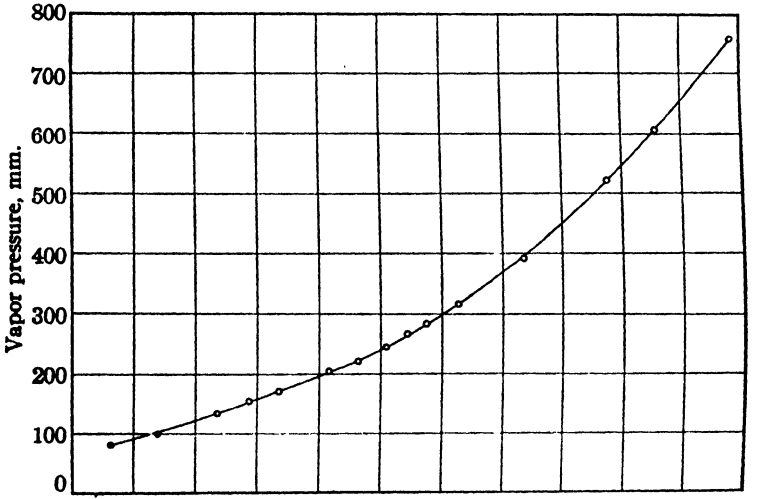

Fig. 1.

Boiling Point.—The Cottrell boiling point on cut 4 was 9.4° (760 mm.). This temperature remained constant for two-thirds of the distillation, which was started with 30 cc. of hydrocarbon.

Freezing Point.—A temperature–time curve on cut 4 indicated its freezing point to be −19.5° (corr.).

Density.—The density of cut 4 was d_0^0 0.613.

Molecular Refraction.—Calcd. for C_5H_{12}, 25.12; obs., 25.36.

Vapor Pressure *vs.* Temperature.—The apparatus consisted of a long-necked 10-cc. flask connected to one arm of a mercury gage which was provided with bulbs at the top of the two arms. The other arm of the gage led to a 10-gallon carboy which was connected to a vacuum pump, a mercury manometer and to the atmosphere. The temperature in the Dewar flask which surrounded the flask was maintained fairly constant by mixtures of ice and hydrochloric acid and acetone and solid carbon dioxide. The temperature in the flask was observed by means of an alcohol thermometer whose

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(12) Whitmore and Lux, This Journal, 54, 3451 (1932).

bulb was immersed completely in the liquid. The accuracy of this apparatus was determined by measuring the vapor pressure of acetone at 0°. The value found was 71.5 mm. compared to the "I. C. T." value of 72.0 mm.

The flask and connection to the mercury gage were freed from air by boiling, and in doing so the vapor was pulled through the gage. With neopentane the system was boiled out six times, the last three readings being constant.

OBSERVED VAPOR PRESSURES AT DIFFERENT TEMPERATURES

Temperature, °C.	9.4	3.1	−1.0	−8.0	−13.4	−15.8	−17.2	−17.6
Vapor press., mm.	760.0	605.7	523.7	394.0	316.5	286.9	276.0	269.5
Temperature, °C.	−19.4	−21.7	−24.0	−28.1	−30.5	−33.1	−38.0	−42.0
Vapor press., mm.	247.0	222.0	206.1	172.1	155.6	135.1	104.6	87.1

Figure 1 shows the vapor pressure *vs.* temperature plot, and Fig. 2, the log vapor pressure *vs.* reciprocal absolute temperature.

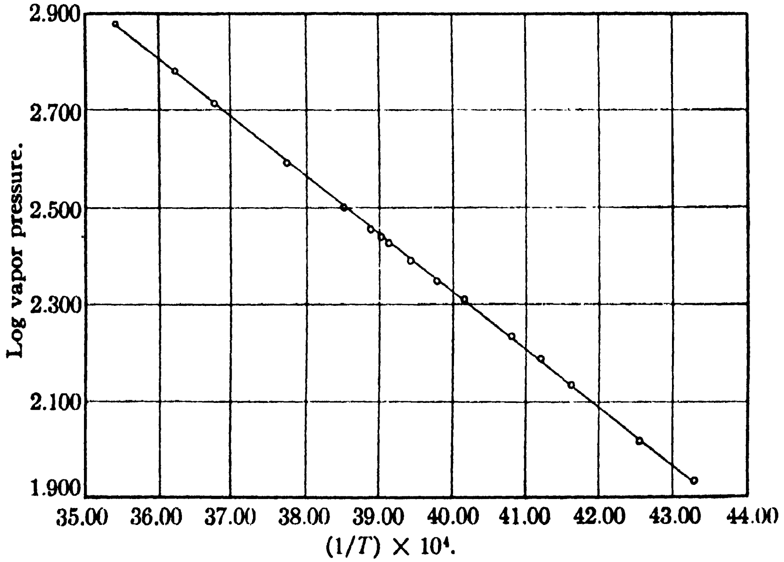

Fig. 2.

Summary

1. A practical method has been developed for making tetramethylmethane (neopentane) in quantity.
2. The physical properties of neopentane have been studied.

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Hexamethylethane

BY FRANK C. WHITMORE, C. J. STEHMAN AND JOHN M. HERNDON

Since hexamethylethane contains two neo carbon atoms it is of particular interest in the field of intramolecular rearrangements.[1] Because the literature contains no satisfactory method for the preparation of this substance, an extended study has been conducted on this subject and the present paper contains two satisfactory methods for its preparation. The study of the halogenation products of hexamethylethane is in progress in this Laboratory.

Experimental

The summary of the methods tried in the work on the preparation of hexamethylethane follows.

		Yield of hexamethylethane, %
1	Ether solution of *tert*-butylmagnesium bromide added to *tert*-butyl chloride	4
2	Ether solution of *tert*-butylmagnesium bromide added to a parafin oil solution of *tert*-butyl chloride	0
3	Ether solution of *tert*-butylmagnesium chloride added to an ether solution of tetramethylethylene dibromide	0
4	Ether solution of *tert*-butylmagnesium chloride added to a cooled, well-stirred suspension of silver bromide in dry ether	18–19
5	*Tert*-butyl chloride added to sodium pellets in ether	0
6	*Tert*-butyl chloride added to a xylene solution of *tert*-butylmagnesium chloride heated to 50°	0
7	Mercuric chloride added to an ether solution of *tert*-butylmagnesium chloride and *tert*-butyl chloride	0
8	Cupric chloride added to an ether solution of *tert*-butylmagnesium chloride	0
9	Ether solution of pentamethylethyl chloride added to an ether solution of methylmagnesium chloride	3
10	Xylene solution of pentamethylethyl bromide added to a xylene solution of methylmagnesium chloride, heated to 60°	10
11	Xylene solution of pentamethylethyl bromide added to a xylene solution of zinc dimethyl	50

In addition, hexamethylethane as a by-product in reactions involving an ether solution of *tert*-butylmagnesium chloride has been obtained with the following reagents in ether solution: (1) allyl bromide, 8%; (2) acetaldehyde, 7%; (3) *n*-butyraldehyde, 5%; (4) isobutyraldehyde, 4%.

Experimental

Preparation of Hexamethylethane

A. By Reaction of Pentamethylethyl Bromide with Dimethylzinc.—Pentamethylethyl alcohol[2] was prepared in 25% yield from *tert*-butylmagnesium chloride and purified acetone. The corresponding bromide[3] was prepared in 85% yield by the reaction of hydrogen bromide with pentamethylethyl alcohol in cold ether solution.

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(1) Whitmore and co-workers, THIS JOURNAL, 54, 3274, 3431, 3435, 3714 (1932).

(2) Edgar, Calingaert and Marker, *ibid.*, 51, 1483 (1929).

Dimethylzinc was prepared by the method of Noller[4] and distilled at atmospheric pressure.

Eight grams (0.084 mole) of dimethylzinc in 50 cc. of xylene was placed in a 500-cc. 3-necked round-bottomed flask fitted with a 100-cc. dropping funnel, a mechanical stirrer, reflux condenser and a thermometer well. The flask was surrounded by a water-bath. Twenty-eight grams (0.16 mole) of pentamethylethyl bromide in 56 cc. of dry xylene was added from the dropping funnel during three hours to the well-stirred solution of dimethylzinc in xylene kept at 32°. This temperature was maintained almost entirely by the heat of the reaction. A few minutes after all of the bromide had been added the reaction was complete as evidenced by a fall in temperature. The mixture was then heated to 43° for fifteen minutes, after which a mixture of 70 cc. of water and 15 cc. of concentrated hydrochloric acid was added in ten minutes from the dropping funnel to decompose any excess dimethylzinc.

The xylene and water layers were separated and the xylene layer dried over 20 g. of anhydrous potassium carbonate for twenty-four hours. A rapid distillation was then made through a 70 × 1.1 cm. indented column[5] equipped with a heating unit on the side arm. The following fractions were collected at 740 mm.: 1, b. p. 75–85°, 2.8 g., $n^{20°}_{D}$ 1.4067; 2, b. p. 85–98°, 1.2 g., $n^{20°}_{D}$ 1.4112; 3, 98–119°, 11.3 g. (solid at room temperature); 4, 119–130°, 4 g., partly solid. The residue of xylene was 80 g. Fractions 2 and 3 combined and cooled in ice–salt mixture gave 9.0 g., 50% yield of hexamethylethane, m. p. 101°. A lowering of the melting point resulted when this material was mixed with a sample of the solid alcohol hydrate and with a sample of pentamethylethyl bromide.

B. By Reaction of Tert-butylmagnesium Chloride with Silver Bromide.—This type of reaction has been run previously and the silver bromide used in this experiment was prepared accordingly.[6]

This preparation of *tert*-butylmagnesium chloride was recently described.[7]

In a 2-liter round-bottomed flask, fitted with a mechanical stirrer, dropping funnel, reflux condenser arranged for the collection of gases, surrounded by an ice–salt bath, was placed 93.9 g. (0.5 mole) of silver bromide and 200 cc. of dry ether. Vigorous stirring was started and an ether solution (volume 190–200 cc.) of 0.5 mole of *tert*-butylmagnesium chloride was slowly added from the dropping funnel. After the first few cc. of the Grignard solution was added the black precipitate of silver could be seen and the ether began to reflux. The remainder of the Grignard reagent was then added at such a rate that a gentle refluxing was maintained. When the reaction was complete, all of the Grignard reagent added and the ether no longer refluxed, the reaction mixture was poured on 1.5 kg. of cracked ice contained in a 3-liter flask. As soon as the reaction mixture was added to the ice the 3-liter flask was securely stoppered until the separation of the phases was complete. The ether layer was removed and kept in a closed container during the extraction of the aqueous portion with 200 cc. of ether. The combined ether portions were dried over 20 g. of anhydrous potassium carbonate. After the careful removal of the ether through a 90 × 2.2 cm. glass-packed column[8] the remaining oil was quickly transferred and distilled through a 68 × 1.1 cm. indented column. The forerun was collected as one fraction 2.0 g. up to 92° when the hexamethylethane began to solidify in the head of the column. The flask was then cooled and the hexamethylethane solidi-

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(3) Henry, *Bull. Acad. Roy. Belg.*, 352 (1906); *Chem. Zentr.*, II, 748 (1906).

(4) Noller, THIS JOURNAL, 51, 594 (1929).

(5) Whitmore and Church, *ibid.*, 54, 3711 (1932).

(6) Gardner and Borgstrom, *ibid.*, 51, 3377 (1929).

(7) Whitmore and Badertscher, *ibid.*, 55, 1561 (1933).

(8) Whitmore and Lux, *ibid.*, 54, 3451 (1932).

fied at room temperature; yield 5.5 g., 19.4%. The yields in 1.0 and 2.0 mole runs were 18 and 13%, respectively.

Summary

1. Practical methods have been developed for making hexamethylethane.

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Some Aspects of the Tschugaeff Reaction for Dehydrating Alcohols[1]

BY FRANK C. WHITMORE AND C. T. SIMPSON[2]

Tschugaeff was the first to suggest the dehydration of alcohols by decomposition of their xanthates.[3] His original paper dealt with the preparation of menthene from menthol, and gave two possible alternative reactions for the decomposition of the xanthate upon heating

$$C_nH_{2n-1}OCS_2R \xrightarrow{\text{Heat}} C_nH_{2n-2} + COS + RSH \qquad (1)$$

$$C_nH_{2n-1}OCS_2R \xrightarrow{\text{Heat}} C_nH_{2n-2} + CS_2 + ROH \qquad (2)$$

It has since been found that (1) is the reaction. The yield is best when R is methyl.

By the same method Tschugaeff[4] also prepared thujene from thujyl alcohol, limonene from carvone, cholesterylene from cholesterylin, and bornylene from borneol. Others have extended the application of the method. Gandurin[5] prepared guajene from guajol. Kurssanoff[6] dehydrated benzhydrol to give tetraphenylethylene and phenylcyclohexylcarbinol to give benzylidene cyclohexane.

In the aliphatic series Fomin and Sochanski[7] prepared tertiary-butylethylene from pinacolyl alcohol. More recently Stevens[8] dehydrated *dextro*-2-methyl-3-ethoxybutanol-2 to secure *dextro*-3-ethoxy-2-methylbutene-1.

In all these preparations the general method was the same. Sodium or potassium (preferably the latter) reacted with the alcohol in a solvent such as xylene. Carbon disulfide was added to form the xanthate of the metal, which was then converted to the methyl xanthate by refluxing with methyl iodide or sulfate. The methyl xanthate gave the olefin when strongly heated.

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(1) Presented before the Organic Division, American Chemical Society, March 28, 1933.

(2) Submitted in partial fulfilment of the requirements for the M.S. degree.

(3) Tschugaeff, *Ber.*, **32**, 3332 (1899).

(4) Tschugaeff, *ibid.*, **33**, 3118, 735 (1900); **34**, 2276 (1901); **37**, 1481 (1904); **42**, 4631 (1909); **45**, 1293 (1912); *Ann.*, **375**, 288 (1910); **388**, 280 (1912).

(5) Gandurin, *Ber.*, **41**, 4362 (1908).

(6) Kurssanoff, *Chem. Centr.*, I, 997 (1921); *Ber.*, **64**, 2297 (1931).

(7) Fomin and Sochanski, *ibid.*, **46**, 246 (1913).

(8) Stevens, THIS JOURNAL, **54**, 3736 (1932).

Apparently in all these instances only the normal dehydration product was formed, that is, no rearrangement took place. The method thus appeared satisfactory for certain secondary and tertiary alcohols, but it was untried for primary alcohols until the present research. It has now been found to give normal dehydration here also. It is suitable for the preparation of pure isopropylethylene from isoamyl alcohol and of pentene-1 from *n*-amyl alcohol. Capryl alcohol gives a mixture of almost equal parts of octene-1 and octene-2.

The particular advantage of the Tschugaeff method is that it avoids rearrangements. This has been confirmed in the present work by the conversion of isoamyl alcohol to pure isopropylethylene, whereas trimethylethylene is the chief product when isoamyl alcohol is subjected to other methods of dehydration. However, the Tschugaeff method is generally avoided since in the original form it was dangerous and inconvenient. This objection was overcome in the present work by modifying the preparation of the metallic xanthate. This consists in reaction of the alcohol with equimolecular quantities of sodium or potassium hydroxide and carbon disulfide, thus forming the xanthate in one step in a larger yield than is secured by the original method. The best results are obtained when an excess of the alcohol is used, with no other solvent, but by using only equimolecular quantities of the alcohol and a neutral solvent such as a mixture of diethyl ether and carbon tetrachloride the yields are lowered only slightly. This modification makes the Tschugaeff reaction much less hazardous and more practicable than the original method. The following reactions represent the modified reaction

$$\mathrm{ROH + NaOH + CS_2 \longrightarrow H_2O + ROCS_2Na \xrightarrow{MeI} ROCS_2Me \xrightarrow{Heat}}$$
$$\mathrm{Olefin + COS + MeSH}$$

The chief obstacle in applying the method to primary alcohols was found to be the comparatively great stability of the primary xanthates toward heat. They can be distilled *in vacuo*, and even when boiled at atmospheric pressure their decomposition is slow and incomplete, so that only small yields of olefins can be secured. Apparently the secondary and tertiary xanthates are much less stable and, consequently, give better yields of olefins.

Experimental

The alcohols were carefully purified by distillation, and only the purest fractions were used in these experiments. The other liquid chemicals were purified by distillation after drying.

Each of the three alcohols was dehydrated by both the original and the modified

Tschugaeff method, and it was found that the latter gave slightly better yields, as may best be indicated by comparing the yields of xanthates.

The yields of about 15% listed for isopropylethylene and pentene-1 may be regarded as conservative and may be almost doubled by more care in purifying and distilling the products obtained from the decomposition of the xanthates.

Original Tschugaeff Method on Isoamyl Alcohol.—A 2-mole run will be taken as typical of the procedure of this method.

Clean potassium (84 g.) was placed in a 5-liter flask containing 1500 cc. of xylene. The flask was attached to a trident fitted with a mechanical stirrer, a Pyrex reflux condenser and a dropping funnel; then 180 g. of isoamyl alcohol was added dropwise with very vigorous stirring and the mixture was warmed to about 65° to melt the potassium and form tiny beads which reacted vigorously so that the reaction was practically all completed in three hours. Then the mixture was diluted with 1500 cc. of diethyl ether and 305 g. of carbon disulfide added with stirring. After standing overnight the mixture was warmed and stirred for three hours longer, and then 570 g. of methyl iodide was added dropwise and the mixture was stirred and refluxed for six hours. After filtering off the potassium iodide the lower-boiling constituents were removed by distillation and the residual xanthate was distilled at 10 mm. through a 68 × 1.1 cm., indented, total-condensation column.[9] The yellow distillate, b. p. 100–105°, weighed 230 g. Redistillation gave 216 g., b. p. 101–103°, while a third distillation gave 142 g., b. p. 102.5–103° (10 mm.), n_D^{20} 1.5230 and d_4^{20} 1.036.

The material of b. p. 101–103° (216 g.) was heated in a 1-liter flask under a partial-reflux column for seven and one-half hours by a free flame, the distillate being condensed by a copper coil packed in an ice–salt mixture. The undecomposed residue amounting to 43 and 45 g. of colorless distillate was collected. The distillate was purified by three extractions with 40% potassium hydroxide solution and one treatment with 20 cc. of saturated mercuric chloride solution to remove the mercaptan; then it was dried over anhydrous sodium sulfate and distilled through the 68 × 1.1 cm. column. It boiled at 19–20° (740 mm.). It was thus mainly isopropylethylene.

Original Method on *n*-Amyl Alcohol.--Practically the same procedure was followed here as in the case of isoamyl alcohol. For a 2-mole run, 180 g. of alcohol gave 207 g. of xanthate, b. p. 108–108.5° (10 mm.), n_D^{20} 1.5247, d_4^{20} 1.040. After heating for nine hours there remained 66 g. of residue, while the distillate amounted to 50 g. ,which after purification distilled at 28.5–29.0° (735 mm.). This boiling point checks that recently established for pentene-1 by Dykstra, Lewis and Boord.[10]

Original Method on Capryl Alcohol.—261 g. of alcohol gave 98 g. of olefin, distilling at 120.5–121.2° (725 mm.), n_D^{20} 1.4113, after purification by refluxing over sodium. In this case the xanthate could not be distilled because it was found to decompose upon boiling, even at 5 mm. At atmospheric pressure, heating in an oil-bath at 165° gave almost complete decomposition.

Modified Tschugaeff Method on Isoamyl Alcohol.—This was a 1-mole run. In a 2-liter flask were placed 40.5 g. of finely pulverized sodium hydroxide, 89 g. of isoamyl alcohol, 600 cc. of diethyl ether and 50 cc. of carbon tetrachloride. The flask was attached to the same apparatus as in the original method, and the mixture was stirred for half an hour to dissolve part of the base and form a finely divided suspension of the remainder. Then 76 g. of carbon disulfide was added during one hour, with the temperature below 30°. After three hours of stirring, 149 g. of methyl iodide was added dropwise and the mixture was stirred and refluxed for six hours longer. The remainder of the procedure was the same as for the original method described above. Distillation of the xanthate gave 126 g., b. p. 100–102° (10 mm.), n_D^{20} 1.5234.

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(9) Whitmore and Lux, THIS JOURNAL, 54, 3451 (1932).

(10) Dykstra, Lewis and Boord, *ibid.*, 52, 3396 (1930).

A run using potassium hydroxide gave the same yield. Still another run, using no other solvent than excess isoamyl alcohol, gave slightly higher yields than when ether and carbon tetrachloride were used as solvents.

Modified Method on *n*-Amyl Alcohol.—From 90 g. of alcohol was obtained 112 g. of xanthate, b. p. 105–107.5° (10 mm.), n^{20}_{D} 1.5253. The olefin boiled at 29° (740 mm.).

Modified Method on Capryl Alcohol.—This was a 2-mole run using 260 g. of capryl alcohol which had been distilled through the 16-meter column;[11] 134 g. of crude olefin was secured by decomposing the crude xanthate. The residue was practically all capryl alcohol. The olefin was purified as usual. The distillate boiled at 120–122° (738 mm.), n^{20}_{D} 1.4115, and weighed 108 g. This was allowed to stand over sodium for several days and was distilled through the 90 × 2.1 cm. partial condensation column built by Franklin Johnston and described in a paper by Whitmore and Lux.[12]

No definite cuts could be obtained, but 12 g. of n^{20}_{D} 1.4095 and 23 g. of n^{20}_{D} 1.4143 were obtained at the lower and upper extremes, respectively. These two fractions were identified by ozonolysis, etc.,[13] as containing octene-1 and octene-2, as follows. The aldehydes secured by decomposing the ozonides were identified by mixed melting points of their semicarbazones and 2,4-dinitrophenylhydrazones with known samples of these same derivatives made from pure heptaldehyde and pure hexaldehyde kindly supplied by John M. Herndon[13] of this Laboratory.

The Tschugaeff reaction applied to capryl alcohol thus gave a mixture of octene-1 and octene-2 of n^{20}_{D} 1.4115, which represents a mixture of about 47% octene-2 and 53% octene-1, according to data supplied by Mr. Herndon, who found octene-1 had n^{20}_{D} 1.4149 and octene-2 n^{20}_{D} 1.4085.

Summary

1. Isoamyl alcohol, *n*-amyl alcohol and capryl alcohol have been dehydrated by the Tschugaeff method.
2. Isoamyl alcohol gave isopropylethylene, *n*-amyl alcohol gave pentene-1 and capryl alcohol gave a mixture of equal parts of octene-2 and octene-1.
3. Primary xanthates are much more stable to heat than are secondary and tertiary xanthates.
4. An advantageous modification of the Tschugaeff technique has been developed.

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[11] Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[12] Whitmore and Lux, THIS JOURNAL, **54**, 3453 (1932).

[13] *Cf.* Whitmore and Herndon, *ibid.*, **55**, 3428 (1933).

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Dehydroperillic Acid, an Acid from Western Red Cedar (Thuja Plicata Don)[2]

BY ARTHUR B. ANDERSON AND E. C. SHERRARD

A compound $C_{10}H_{12}O_2$ was isolated from western red cedar heartwood by Blasdale[3] in 1907. He describes this compound as being a white crystalline substance melting at 80° and having a cedar-like odor. In 1929 Sherrard and Sondern[4] also isolated a compound $C_{10}H_{12}O_2$ from western red cedar, which they reported as being an acid and melting at 86.5°. The present authors have isolated two compounds from cedar, one being an acid $C_{10}H_{12}O_2$ which when pure is odorless and melts at 88°. The other compound to which we also assign the formula $C_{10}H_{12}O_2$ (tentative) is a white crystalline substance, m. p. 82°, having a slight odor and which seems to be phenolic. In that Blasdale was only able to give a melting point and an empirical formula of the compound, it is not known which of the above compounds he has isolated. We have obtained the acid in sufficient quantities so that we are able to propose a structural formula as a result of a series of reactions carried out at the Forest Products Laboratory.

Sowder[5] has shown that the water extractives obtained from western red cedar are very toxic to the wood-destroying fungus *Lentinus lepideus*, but no direct evidence has been reported as to the actual chemical nature of the toxic principle or principles in western red cedar. The phenolic compound that we have isolated from cedar is very toxic to *Fomes annosus*. A concentration of 0.005 to 0.007% of this compound in agar is sufficient to kill or inhibit the growth of this wood-destroying fungus. It is about ten times more toxic than creosote to this particular organism. This compound, undoubtedly, is one of the toxic compounds that renders western red cedar wood so resistant to decay. A report on the experimental work on the determination of the formula of this phenolic compound and a detailed study of its toxic properties will appear in a subsequent publication. This paper will be concerned with the evidence we have obtained in support of the structural formula for the new acid, $C_{10}H_{12}O_2$. This compound is non-toxic but seems to have a slight corrosive reaction to iron and copper.

Dehydroperillic acid, as we propose to call it for reasons given below, was isolated from western red cedar sawdust by steam distillation. The

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(1) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

(2) Submitted to the Graduate School at the University of Wisconsin, Madison, Wis., by Arthur B. Anderson in partial fulfilment for a Ph.D. degree in chemistry.

(3) Blasdale, THIS JOURNAL, **29**, 539 (1907).

(4) Sherrard and Sondern, unpublished report, Forest Products Laboratory, Madison, Wis., September, 1929.

(5) Sowder, *Ind. Eng. Chem.*, **21**, 981 (1929).

melting point of the acid has been raised to 88°, but the empirical formula originally assigned to it has been confirmed. The white crystalline acid, when kept in glass-stoppered bottles over a period of several weeks, gradually becomes yellow and acquires a strong odor but can be readily repurified by redistilling with steam. It will remain colorless for a long period of time in a vacuum desiccator over concentrated sulfuric acid.

The acid is insoluble in cold water and forms an insoluble oil in hot water. It is readily soluble in ether, acetone, alcohol, ethyl acetate, chloroform and acetic acid. It is optically inactive in either acetone or alcohol. It decolorizes potassium permanganate immediately and slowly reacts with bromine in chloroform solution, but forms no definite product with the latter.

Dehydroperillic acid, when refluxed with 3% hydrochloric acid solution using dilute acetic acid as a solvent, was quantitatively converted into an isomeric compound, cuminic acid (*p*-isopropylbenzoic acid). It absorbed 3 moles of hydrogen on catalytic hydrogenation, using palladium black as a catalyst. The compound can also be reduced with sodium, in either ethyl or amyl alcohol, but no definite product could be isolated. The acid forms a liquid methyl ester which readily solidifies, m. p. 34.5°. Upon hydrolyzing the ozonide, formaldehyde, formic acid, acetaldehyde, acetic acid, oxalic acid, carbon dioxide and probably β,γ-diketovaleric acid were obtained.

Experimental

Isolation and Purification of Dehydroperillic Acid.—Western red cedar heartwood sawdust was distilled with steam in a copper cylinder, capacity about 5 kg. The distillation was continued until the distillate was no longer acid to litmus (approximately 100 liters). The first 20 liters of the distillate was quite cloudy, a very small amount of volatile oil finally settling at the bottom. After separating the volatile oil, the total distillate was made alkaline with a concentrated barium hydroxide solution. The yellow precipitate that formed was filtered off, the barium salt of the acid being soluble. Twenty-liter portions of the alkaline distillate were then reduced to a volume of about 300 cc. in large evaporating dishes over a gas flame (the acid is very stable in alkaline solution). After cooling, the concentrated solution was filtered and the resulting clear, yellow filtrate was acidified with dilute hydrochloric acid. After standing a short time, large, flake-like crystals were obtained which were recovered by filtration with suction. Since they were contaminated by a slight brownish impurity, they were purified by solution in sodium bicarbonate and filtered from the insoluble gummy residue. The acid was reprecipitated by acidifying with dilute hydrochloric acid. After repeating this procedure several times a nearly colorless crystalline substance was obtained which was finally purified by steam distillation. The acid obtained in this manner has a melting point of 88°. The yield of the acid varied greatly, depending upon the portion of the tree from which the sawdust was obtained; yields on the basis of oven-dry wood varied from 0.03 to 0.30%.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.13; H, 7.37. Found: C, 73.10, 72.90, 72.81; H, 7.25, 7.41, 7.35. *Mol. wt.* Calcd. for $C_{10}H_{12}O_2$: 164.1. Found: 163.8, 165.2 (neut. equiv.); by cryoscopic method (Rast), 170.

Methyl Ester.—The ester was prepared by refluxing 7 g. of the silver salt of the acid with 65 g. of methyl iodide for five hours. The ester was isolated in the usual manner. The yield was practically quantitative. The ester thus obtained was a colorless liquid having a pleasant odor; b. p. (14 mm.) 112–113°; d_4^{22} 1.0225; n_D^{22} 1.5130; *M*R calcd., for $C_{11}H_{14}O_2$ and 3F, 51.154; *M*R found, 52.354.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.11; H, 7.92. Found: C, 73.90; H, 7.91.

The ester can be solidified readily by scratching the walls of the tube containing the ester with a glass rod, the entire liquid immediately solidifying, m. p. 34.5 to 35.0°. Upon saponifying either the liquid or solid ester with alcoholic potassium hydroxide and liberating the acid with dilute sulfuric acid, dehydroperillic acid was again obtained, m. p. 88°.

Cuminic Acid (*p*-Isopropylbenzoic Acid).—About 1 g. of dehydroperillic acid was heated under a reflux condenser with 15 cc. of 3% hydrochloric acid. After the mixture began to boil just enough glacial acetic acid was added to dissolve the acid. After boiling for thirty minutes the reaction mixture was poured into cold water, causing the precipitation of small white needles. Recrystallization from hot water gave a colorless crystalline compound, m. p. 116°. This acid no longer decolorized a chloroform solution of bromine, nor did it oxidize in the presence of cold alkaline potassium permanganate. It had the same empirical formula $C_{10}H_{12}O_2$ as dehydroperillic acid. This isomeric compound thus formed gave no depression of the melting point when mixed with cuminic acid, which was prepared according to R. Meyer's[6] method from cuminal with potassium permanganate. For further confirmation the nitro-[7] and hydroxy-[8] derivatives of cuminic acid were prepared and compared with the corresponding derivatives of the substance obtained from dehydroperillic acid. The nitro derivative of each of the above compounds alone and mixed melted at 156–157°. Likewise, the hydroxy derivative alone and mixed melted at 155–156°. Therefore it is apparent that dehydroperillic acid is rearranged by aqueous hydrochloric acid to form the isomeric compound cuminic acid.

Catalytic Reduction of Dehydroperillic Acid.—A solution of 1 g. of dehydroperillic acid in 10 cc. of alcohol was added to an alcoholic suspension of palladium black which had been previously reduced. The whole was shaken in hydrogen, of which 450 cc. was absorbed in twenty-five minutes and no further absorption took place (calcd. for 3 mols. at 22° and 740 mm., 467 cc.). The catalyst was filtered off and the alcohol removed under reduced pressure. The liquid residue was taken up in ether and dried over anhydrous sodium sulfate. This was filtered and the ether removed under reduced pressure. The colorless liquid that remained distilled at 150 to 152° (16 mm.); d_4^{25} 0.9925; n_D^{25} 1.4670; *M*R calcd. for $C_{10}H_{18}O_2$, 47.71; *M*R found, 47.56.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.58; H, 10.67. Found: C, 70.49; H, 10.61

The reduced product did not decolorize a dilute alkaline potassium permanganate solution, indicating that the compound $C_{10}H_{18}O_2$ is saturated and therefore must contain one cycle. This compound, to our knowledge, has never been reported. We believe it to be the liquid isomer of hexahydrocuminic acid. The solid isomer of hexahydrocuminic acid has been prepared by Markownikoff.[9]

Preparation and Hydrolysis of the Ozonide.—Dehydroperillic acid (10.46 g.) was dissolved in 100 cc. of absolute ethyl acetate, and the solution cooled in a salt–ice mixture. A current of oxygen containing about 4 to 5% ozone was passed through the solution at a velocity of 18 liters per hour for twelve hours. The ethyl acetate was then

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(6) Meyer, *Ann.*, **219**, 243 (1883).
(7) Cahours, *ibid.*, **69**, 243 (1849).
(8) Meyer, *Ber.*, **11**, 1284 (1878).
(9) Markownikoff, *J. prakt. Chem.*, [2] **57**, 95 (1898).

distilled off under reduced pressure in the presence of carbon dioxide at 15°. The resulting ozonide was a very heavy, nearly colorless liquid. Previous trials with chloroform as a solvent gave a waxy ozonide, which did not hydrolyze as readily as the ozonide prepared in the above manner.

The ozonide thus obtained, together with 120 cc. of water, was put into a flask provided with a reflux condenser. The latter was successively connected with three flasks, the one (A) containing 100 cc. of cold water, and the other two (B and C) each containing 400 cc. of 0.2 *N* barium hydroxide solution in order to retain any volatile and gaseous products that might be formed during the decomposition. The flask was carefully warmed on a water-bath while a current of hydrogen was passed slowly through the whole apparatus. After several hours of careful heating the ozonide was completely decomposed, leaving a light red solution.

In flasks B and C barium carbonate was precipitated. After filtering off the precipitate, the excess of barium hydroxide was titrated with standardized sulfuric acid. The quantity of carbon dioxide amounted to 1.54 g.

The solution in flask A was decidedly acidic as well as aldehydic in reaction. An acetic acid solution of *p*-nitrophenylhydrazine was added to a small portion of the solution and a yellow precipitate immediately formed. After filtration and recrystallization from alcohol a crystalline substance was obtained, m. p. 128°, which produced no depression of the melting point when mixed with the *p*-nitrophenylhydrazone of acetaldehyde. The remainder of the solution in flask A was neutralized with *N*/10 sodium hydroxide solution, the amount of alkali consumed for neutralization corresponded to 0.66 g. of acid, calculated as formic acid. This alkaline solution was very carefully distilled; the first portion of the distillate was decidedly volatile. To this an acetic acid solution of *p*-nitrophenylhydrazine was added, forming a precipitate. This was filtered off and recrystallized from alcohol, yielding a crystalline substance, m. p. 180°, which produced no depression of the melting point when mixed with the *p*-nitrophenylhydrazone of formaldehyde. The alkaline solution in the distilling flask was acidified with dilute sulfuric acid and distilled. This distillate gave the following characteristic reactions of formic acid: (1) reduced a neutral silver nitrate solution, (2) formed an insoluble precipitate of mercurous chloride when heated with a solution of mercuric chloride, and (3) formed a black metallic mercury precipitate when subjected to the mercuric oxide test.

The hydrolyzed solution of the ozonide was next steam distilled. The distillate, which was acidic, was neutralized with sodium hydroxide solution and distilled. No aldehydes or ketones could be detected in the distillate. The alkaline solution was evaporated to dryness, acidified with sulfuric acid and distilled. The fraction distilling below 105° was identified as formic acid. The fraction distilling above 105° was identified as acetic acid, by preparing its *p*-nitrobenzyl ester, m. p. 78°.

The non-volatile portion of the hydrolyzed ozonide was concentrated to a sirup at 35° under reduced pressure. This sirup upon cooling partially solidified. The crystals were filtered off and dried on a porous plate. The substance melted at 100°, and gave no depression of the melting point when mixed with oxalic acid. The liquid that remained after filtration was diluted with water. To a portion of this aqueous solution an acetic acid solution of *p*-nitrophenylhydrazine was added, forming a dark red precipitate. This was filtered off and washed well with water. The dark red precipitate was then dried in a vacuum desiccator containing solid potassium hydroxide and concentrated sulfuric acid, m. p. 294–295° (with decomposition).

Anal. (Micro) 5.315 mg. gave 0.040 mg. of ash or 0.75%; 4.303 mg. gave 0.784 cc. of N_2 at 23° and 743 mm.; 4.915 mg. gave 0.904 cc. of N_2 at 24° and 732 mm. Calcd. for $C_{17}H_{16}N_6O_6$, N, 20.99. Found: N, 20.54, 20.31. The amount available was too small for further purification.

The melting point (295°) of this compound corresponds to the *p*-nitrophenylosazone of β,γ-diketovaleric acid prepared by Harries and Kircher.[10] The acid also formed a green copper salt with copper acetate, similar to the one described by Harries for β,γ-diketovaleric acid.

To the remainder of the aqueous solution of the ketonic acid an acetic acid solution of *p*-bromophenylhydrazine was added which soon formed a precipitate. This was filtered, recrystallized from alcohol, and dried, m. p. 220°. This compound was ash free.

Anal. (Micro) 2.865 mg. gave 0.308 cc. of N_2 at 23° and 731 mm.; 2.087 mg. gave 0.219 cc. of N_2 at 23° and 731 mm.; 2.551 mg. gave 0.276 cc. of N_2 at 23° and 731 mm.[11] Calcd. for the *p*-bromophenylosazone of β,γ-diketovaleric acid, $C_{17}H_{16}N_4O_2Br_2$, N, 11.98. Found: N, 11.89, 11.60, 11.95.

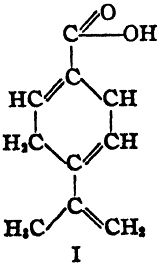
The analysis indicates that this compound is probably β,γ-diketovaleric acid.

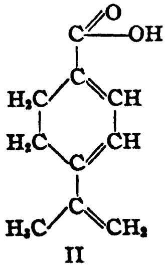
Thus, the following compounds were obtained as the result of the hydrolysis of the ozonide prepared from dehydroperillic acid, formaldehyde, formic acid, acetaldehyde, acetic acid, oxalic acid, carbon dioxide and probably β,γ-diketovaleric acid.

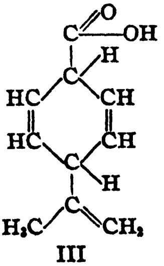
Discussion

Since the acid $C_{10}H_{12}O_2$ is so readily converted quantitatively into the isomeric compound, cuminic acid, and since it contains three double bonds as was established by catalytic hydrogenation, we propose the paramenthane structure as the underlying carbon skeleton of the acid. Consequently, the saturated acid obtained by the above method would be the liquid isomer of the solid hexahydrocuminic acid prepared by Markownikoff.[9]

The identification of formaldehyde and formic acid among the products of hydrolysis from the ozonide implies the presence of a terminating methylene group somewhere in the molecule. The paramenthane carbon structure has three terminating carbon atoms. The only two with which we are concerned, however, are carbon atoms 7 and 9. Because carbon atom 7 is in the form of a carboxyl group, the terminating double bond could only be between carbon atoms 8 and 9. Excluding optically active formulas, there are three possible structures having a terminating methylene group, namely,


I


II


III

The only compound with the foregoing structures that would yield β,γ-diketovaleric acid as the result of the hydrolysis of its ozonide would be

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(10) Harries and Kircher, *Ann.*, **374**, 353–356 (1910); *Ber.*, **40**, 1651 (1907).

(11) The authors are indebted to Dr. E. Schoeffel, of the University of Wisconsin, for the above microanalysis.

structure No. I. Should oxalic acid be of any diagnostic value in determining the structure of the compounds above, it would suggest structure II as being correct. However, since these compounds are so highly unsaturated, the formation of oxalic acid is probably of no direct value in determining the position of the double bonds. The formation of acetaldehyde and acetic acid could arise from the further degradation of either oxalacetic acid, semialdehyde of malonic acid, malonic acid or β,γ-diketovaleric acid.

The further establishment of conjugated double bonds thus excluding structure III was evident from the molecular refraction exaltation observed from the methyl ester of the acid. The observed molecular refraction was 52.354, as compared with the calculated value, 51.154, for $C_{11}H_{14}O_2$ containing three double bonds. Further evidence of α,β-unsaturation or conjugated double bonds was suggested by the ease with which dehydroperillic acid reduced with sodium in the presence of either ethyl or amyl alcohol.

A careful investigation of the chemical literature indicates that no compound with the properties here described has been previously reported. We are convinced, therefore, that the acid described is new and suggest structure I for it. Since it has one more double bond than perillic acid, we propose to call it dehydroperillic acid (4 isopropylene-Δ^{3-6}-cyclohexadiene-1-carboxylic acid), in conformity with the name "dehydrogeranic acid" proposed by Cahn, Penfold and Simonsen,[12] for the olefinic acid $C_{10}H_{14}O_2$, which was isolated in the form of its geranyl ester from *Callitropsis araucarioides*.

With the exception of dehydrogeranic acid, dehydroperillic acid is probably the most highly unsaturated acid, containing as few as ten carbon atoms isolated from nature. To our knowledge this is the first menthatriene derivative that has been found to occur in nature.

The authors wish to acknowledge their indebtedness to J. Alfred Hall, Biochemist of the Forest Products Laboratory, for advice and criticism received throughout the course of this investigation.

Summary

The isolation of a new acid, dehydroperillic acid, from the heartwood of western red cedar is described. Experimental results show that this compound is an isomer of cuminic acid and a structural formula is suggested.

The methyl ester of dehydroperillic acid is described. It is a convenient derivative for identification. The liquid isomer of hexahydrocuminic acid is also described.

A toxic compound (tentative $C_{10}H_{12}O_2$) has been isolated from western red cedar, the identification of which is now being carried out at the Forest

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[12] Cahn, Penfold and Simonsen, *J. Chem. Soc.*, 3134–3142 (1931).

Products Laboratory, along with a detailed study of its toxicity to various wood-destroying fungi.

MADISON, WISCONSIN

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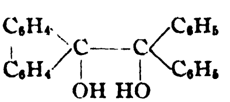
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Pinacol–Pinacolone Rearrangement. IV. The Rearrangement of Pinacols Containing the Biphenylene Group

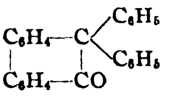
BY W. E. BACHMANN AND HELEN R. STERNBERGER[1]

Meerwein[2] found that diphenylbiphenyleneglycol (I) on treatment with sulfuric acid gives 10,10-diphenylphenanthrone (II) but does not give any of the isomeric benzoylphenylfluorene (III) by migration of the phenyl



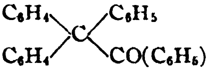
$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!\underset{OH}{C}\text{---}\underset{HO}{C}\!<\!\begin{matrix}C_6H_5\\ \\C_6H_5\end{matrix}$$

(I)



$$\begin{matrix}C_6H_4\text{---}C\!<\!\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\\|\qquad\ \ |\\C_6H_4\text{---}CO\end{matrix}$$

(II)



$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_5\\ \\CO(C_6H_5)\end{matrix}$$

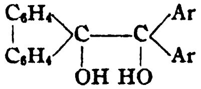
(III)

group. Recently, Bergmann and Schuchardt[3] observed that dehydration by acetyl chloride gives benzoylphenylfluorene (III) and no diphenylphenanthrone. Furthermore, their discovery that benzoylphenylfluorene is isomerized into diphenylphenanthrone by sulfuric acid makes it appear probable that benzoylphenylfluorene is the true product of the rearrangement.

We find that diphenylbiphenyleneglycol (I) when treated with acetyl chloride actually gives a mixture of diphenylphenanthrone and benzoylphenylfluorene and not a single product as has been reported. Similarly,

TABLE I

REARRANGEMENT OF PINACOLS



$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!\underset{OH}{C}\text{---}\underset{HO}{C}\!<\!\begin{matrix}Ar\\ \\Ar\end{matrix}$$

Group Ar	Products	%	Group migrated
Phenyl	Benzoylphenylfluorene	78	Phenyl
	Diphenylphenanthrone	22	Biphenylene
m-Tolyl	*m*-Toluyl-*m*-tolylfluorene	54	*m*-Tolyl
	Di-*m*-tolylphenanthrone	46	Biphenylene
p-Tolyl[4]	*p*-Toluyl-*p*-tolylfluorene	14	*p*-Tolyl
	Di-*p*-tolylphenanthrone	86	Biphenylene
Anisyl[4]	Anisoylanisylfluorene	2	Anisyl
	Dianisylphenanthrone	98	Biphenylene
Phenetyl	*p*-Ethoxybenzoylphenetylfluorene	4	Phenetyl
	Diphenetylphenanthrone	96	Biphenylene

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(1) Presented in partial fulfilment of the requirements for the Ph.D. degree.

(2) Meerwein, *Ann.*, **396**, 200 (1913).

(3) Bergmann and Schuchardt, *ibid.*, **487**, 225 (1931).

(4) Bergmann and Schuchardt obtained a single rearrangement product.

two rearrangement products, corresponding to (II) and (III), are obtained from four other pinacols. The results are presented in Table I.

Giving a value of unity to the migration aptitude of the phenyl group one has the following series representing the relative migration aptitudes of the groups in biphenylene pinacols: phenyl, 1.0; *m*-tolyl, 0.33; biphenylene, 0.31; *p*-tolyl, 0.046; phenetyl, 0.012; anisyl, 0.006. The migration aptitudes of five of these groups, phenyl, *m*-tolyl, *p*-tolyl, phenetyl and anisyl, have been determined when they are situated in symmetrical pinacols.[5] In Table II is given a comparison of the relative migration aptitudes of these five groups in the two types of pinacols.

TABLE II

MIGRATION APTITUDES

Group	M_s (symmetrical pinacol)	M_b (biphenylene pinacol)	$1/M_b$
Phenyl	1.0	1.0	1.0
m-Tolyl	1.95	0.33	3.0
p-Tolyl	15.0	.046	22
Phenetyl	66	.112	83
Anisyl	70+	.006	170

It is observed that the order in the two series is exactly reversed; moreover, the reciprocals of the values for the migration aptitudes in the biphenylene pinacols are roughly of the same order as the values for the symmetrical pinacols. We are preparing and rearranging a large number of pinacols in order to determine whether the relation holds true for the whole class of biphenylene pinacols.

Experimental

Preparation of the Pinacols.—The pinacols were prepared by the action of a Grignard reagent on the methyl ester of biphenyleneglycolic acid.[1,4] A solution of 15 g. of the methyl ester was added to the Grignard reagent which had been prepared from 0.25 gram mole of aryl halide (*m*-bromotoluene, *p*-bromophenetole, etc.). After being refluxed for twelve hours the mixture was hydrolyzed. In this manner, dianisylbiphenyleneglycol, prepared by Bergmann and Schuchardt in 37% yield, was obtained by us in 80% yield. The yields and properties of the two new pinacols, di-*m*-tolylbiphenyleneglycol and diphenetylbiphenyleneglycol, are given in Table III.

Rearrangement of the Pinacols.—The pinacols were rearranged by a twenty-four hour treatment with acetyl chloride in benzene and acetic acid.[6] This agent does not isomerize benzoylphenylfluorene.

Analysis of Pinacolone Mixtures.—The mixture of benzoylphenylfluorene and diphenylphenanthrone from 3.64 g. (0.01 mole) of diphenylbiphenyleneglycol was heated with a solution of 6 g. of potassium hydroxide in 100 cc. of absolute alcohol for six hours. This process cleaved the benzoylphenylfluorene into benzoic acid and phenylfluorene but left the diphenylphenanthrone unchanged. Five separate runs gave an average of 0.0070 gram mole of benzoic acid. This represents a 78% migration of the phenyl group since a 95% yield of total products was obtained and a 95% yield of benzoic acid resulted by scission of pure benzoylphenylfluorene.

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(5) Bachmann and Moser, THIS JOURNAL, 54, 1124 (1932), and unpublished results.

Practically the same results were obtained when both the benzoylphenylfluorene and the diphenylphenanthrone were cleaved, the latter being converted to 2-benzhydryl-2′-carboxylbiphenyl. The mixture of pinacolones was heated with a solution of 25 g. of potassium hydroxide in 100 cc. of methanol for three days. After removal of the solvent the product was treated with a mixture of water and benzene; potassium benzoate dissolved in the water while the potassium salt of the 2-benzhydryl-2′-carboxylbiphenyl was contained in the benzene layer along with phenylfluorene. Treatment with hydrochloric acid converted the salt to the free acid; when the mixture of phenylfluorene and acid was dissolved in hot *n*-propyl alcohol and the solution was allowed to cool, the phenylfluorene deposited first. The 2-benzhydryl-2′-carboxylbiphenyl was obtained in large colorless prisms; m. p. 175° with previous softening.[6] The potassium salt of the acid is little soluble in dry benzene but dissolves readily in wet benzene or in wet ether; it can be obtained as colorless leaflets by recrystallization from methanol.

The mixtures of pinacolones obtained from the other pinacols were analyzed in a similar manner; the values given in Table I represent the averages of several runs which checked each other closely. Di-*p*-tolylphenanthrone and dianisylphenanthrone are cleaved into the biphenyl acids by six hours of heating with 6% potassium hydroxide in ethanol; the properties of the acids and of other compounds are given in Table III. The yields are based on recrystallized product.

TABLE III

YIELDS AND PROPERTIES OF NEW COMPOUNDS

Compound	Yield, %	M. p., °C.	Recryst. solvents	Cryst. form	Analyses, % Calcd.	Found
Di-*m*-tolylbiphenyleneglycol	55	143.5–144.5	Acetone + alc.	Needles	C, 85.7 H, 6.2	85.2 6.2
Diphenetylbiphenyleneglycol	51	147–150	Acetone + alc.	Cubes	C, 79.6 H, 6.2	79.2 6.1
Di-*m*-tolylphenanthrone	62	198.0–198.5	Acetic acid	Diamond plates	C, 89.8 H, 5.9	89.6 6.0
Diphenetylphenanthrone	77	135.0–135.5	*n*-Propyl alc.	Fine needles	C, 82.9 H, 6.0	83.2 6.4
2-(Di-*p*-methylbenzhydryl)-2′-carboxybiphenyl[a]	76	193–194	*n*-Propyl alc.	Diamond plates	C, 85.7 H, 6.2	85.5 6.2
2-(Di-*p*-methoxybenzhydryl)-2′-carboxylbiphenyl	75	136–137	*n*-Propyl alc.	Heavy needles	C, 79.2 H, 5.7	78.9 6.2

[a] Bergmann and Schuchardt obtained an amorphous solid which they considered to be this acid from the reaction between ditolylphenanthrone and alkali.

Summary

Five pinacols containing the biphenylene group have been rearranged by acetyl chloride to mixtures of pinacolones. The order and extent of migration of the groups is the reverse of the migration aptitudes of the groups in symmetrical pinacols.

ANN ARBOR, MICHIGAN

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PUBLISHED SEPTEMBER 5, 1933

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[6] Compare Acree, *Am. Chem. J.*, **33**, 180 (1905).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Supposed Enolizing Power of Organic Magnesium Compounds

BY E. P. KOHLER AND DONALD THOMPSON

In a paper entitled "Researches on the Enolization of Ketones," Grignard and Blanchon[1] described the formation of a number of halomagnesium enolates by the action of isopropylmagnesium bromide on saturated ketones. In proof that their magnesium derivatives were enolates, they converted them into acetates with acetyl chloride and hydrolyzed the acetates to keto-enol mixtures in which they determined the enol content by the method of Job and Reich.[2]

Since the formation of an acetate by the action of acetyl chloride on a halomagnesium enolate which has no substituent in the alpha position is contrary to our experience,[3] we decided to repeat one of the experiments of Grignard and Blanchon in the hope of discovering the reason for the discrepancy, selecting for this purpose the reaction with cyclohexanone because cyclohexenyl acetate can be prepared by a method that leaves no doubt as to its structure.[4]

We began by operating as nearly as possible in accordance with the directions of the authors, but although we repeated their experiment a number of times, employing carefully purified cyclohexanone and isopropyl bromide, we were unable to isolate any cyclohexenyl acetate. By careful distillation under diminished pressure it was possible to secure a fraction which boiled approximately at the specified temperature, but the boiling point at the ordinary pressure (174–175°) and an analysis showed that this fraction was almost pure cyclohexyl acetate.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found: C, 68.1; H, 10.1.

We then prepared pure cyclohexenyl acetate by the method of Mannich and Hancu and hydrolyzed it as directed by Grignard and Blanchon. But here also, in spite of many attempts, we were unable to duplicate their results; our hydrolysis product was always pure cyclohexanone.

Finally, in order to determine the primary products we added cyclohexanone to isopropylmagnesium bromide as directed, but decomposed the resulting magnesium compounds with ammonium chloride in the ordinary manner. We thus obtained two liquids, the one boiling at 160–161°, the other at 115–116° (2 mm.). The lower boiling liquid was identified as cyclohexanol by its boiling point, its index of refraction (n_D^{20} 1.4660) and the melting point of its phenyl urethan (82.5°). The higher boiling frac-

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(1) Grignard and Blanchon, *Bull. soc. chim.*, [4] **49**, 23 (1931).

(2) Job and Reich, *ibid.*, [4] **33**, 1414 (1923).

(3) Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932); Kohler and Peterson, *ibid.*, **55**, 1073 (1933).

(4) Mannich and Hancu, *Ber.*, **39**, 1594 (1906); **41**, 564 (1908).

tion was identified as cyclohexylidene cyclohexanone by an analysis and a comparison of its semicarbazone (m. p. 177°) with that of an authentic sample. The yields were 34 g. or 68% of cyclohexanol and 11.6 g. or 26% of cyclohexylidene cyclohexanone from 49 g. of the ketone.

From the foregoing account it is evident that under the conditions favored by Grignard and Blanchon, at least 94% of the product of the reaction between cyclohexanone and isopropylmagnesium bromide is composed of substances which are not due to enolization but to reduction and to condensation. Lower temperatures, which according tot he French authors are less favorable to enolization, are in reality less favorable to reduction, the reduction product being in part replaced by the normal addition product. Thus at −5° the yield of cyclohexanol was only 28%.

In view of these results we are compelled to conclude that Grignard and Blanchon were misled by the method of Job and Reich, and that they mistook cyclohexyl acetate for cyclohexenyl acetate, cyclohexanol for cyclohexenol. Grignard reagents containing secondary and tertiary hydrocarbon residues frequently act as condensing and reducing agents, but we can find no evidence that they are more effective than others in inducing enolization, and we also fail to find any evidence that any Grignard reagents can convert mono ketones into enolates unless the hindrance to addition is prohibitive.

Summary

An examination of the reaction between isopropyl magnesium bromide and cyclohexanone showed that Grignard and Blanchon must have mistaken reduction for enolization.

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 29, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Some New Local Anesthetics Containing the Piperazine Ring

BY JOHN H. GARDNER AND JOHN H. SCHNEIDER

As piperazine can be regarded as a double secondary amine, it seemed of interest to prepare and study a series of esters of piperazine-dialkanols, which could be regarded as compounds of the procaine type and therefore would be expected to possess local anesthetic activity. The only compound of this type noted in the literature was β-1,4-piperazine-diethyl benzoate which was described by Pyman. He stated that this substance shows[1] marked local anesthetic activity but is quite toxic.

In the present investigation, β-1,4-piperazine-diethanol and γ-1,4-piperazine-dipropanol were prepared by the condensation of piperazine

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(1) Pyman, *J. Chem. Soc.*, **93**, 1802 (1908).

with ethylene chlorohydrin or with trimethylene chlorohydrin. γ-1,4-Piperazine-dipropyl benzoate was prepared by the action of benzoyl chloride on the corresponding alcohol in pyridine solution. The phenyl urethans were formed by the action of phenyl isocyanate on the alcohols in anhydrous acetone, and the cinnamates were prepared with cinnamoyl chloride in acetone. The hydrochlorides were prepared by treating alcoholic solutions of the esters with hydrogen chloride in alcohol.

No quantitative pharmacological data have as yet been obtained on these compounds, but all show decided local anesthetic activity on the tongue. All of the compounds give rather acid solutions and are precipitated from solution at rather low *P*H values.

Experimental

β-1,4-Piperazine-diethanol.—This was prepared by the method of Pyman.[1]

γ-1,4-Piperazine-dipropanol.—This was prepared in a similar manner, using trimethylene chlorohydrin in place of ethylene chlorohydrin; yield, 48%, m. p. 142–143°.

Anal. Calcd. for $C_{10}H_{22}O_2N_2$: N, 13.88. Found: N, 13.87.

Ester Hydrochlorides.—The yields, properties and composition of the new hydrochlorides are shown in Table I.

TABLE I

-1,4-Piperazine hydrochloride	Yield, %	M. p., °C. corr.	Analyses, % Calcd. Cl	Calcd. N	Found Cl	Found N
β-Diethyl phenylurethan	86	260–261	14.62	11.55	14.50	11.64
β-Diethyl cinnamate	66	261–262	13.98	5.48	13.78	5.60
γ-Dipropyl benzoate	45	251–252	14.69	5.80	14.64	5.74
γ-Dipropyl phenylurethan	52	250–251	13.82	10.91	13.60	10.73
γ-Dipropyl cinnamate	47	254–255	13.16	5.20	13.06	5.24

Summary

Five new esters of piperazine-dialkanols have been prepared. These compounds have been found to be local anesthetics, but to give highly acid solutions.

ST. LOUIS, MISSOURI

RECEIVED MAY 29, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

A Group of Isomeric Esters[1]

BY JOHN R. RUHOFF[2] AND E. EMMET REID

The preparation and investigation of the group of esters having the formula RCOOR′, where R and R′ are normal saturated aliphatic residues, containing fifteen carbon atoms together, were undertaken in connection with other work on the general problem of the relation of structure to physical properties. The present paper describes the synthesis and the determination of the more common physical constants of these compounds. Further physical and chemical studies are being carried on in this Laboratory.

Although certain of these esters have been prepared before, it was felt desirable, in order to make significant comparisons of physical properties, to have samples of comparable purity. All of the fifteen isomers have been made in quantities sufficient (usually 1 mole, 256 g.) to permit of a

TABLE I

PROPERTIES OF THE ISOMERIC ESTERS

C atoms in Alkyl group	C atoms in Acid	B. p., °C. at 30 mm.	M. p., °C.	n_D^{20}	d_4^0	d_4^{25}	Coeff. of exp. × 10^4	M_D^{20} (calcd. 77.62)
1	15	199.0	15.46[h]	1.4390	Solid[l]	0.8618	8.91	77.86
2	14	195.0[a]	11.94[i]	1.4362	Solid[m]	.8573	8.96	77.83
3	13	194.0	− 5.74	1.4357	0.8748	.8555	8.90	77.92
4	12	194.0[b]	− 6.84	1.4354	.8747	.8555	8.91	77.88
5	11	193.0	−21.17	1.4356	.8752	.8560	8.86	77.86
6	10	193.0	−17.67	1.4351	.8743	.8553	8.79	77.85
7	9	192.5[d]	−15.54	1.4350	.8745	.8553	8.87	77.84
8	8	192.5[e]	−18.08[f]	1.4352	.8745	.8554[g]	8.87	77.85
9	7	193.0	−11.14	1.4352	.8745	.8552	8.91	77.87
10	6	193.0	−19.29	1.4353	.8743	.8552	8.82	77.88
11	5	193.5	−23.14	1.4358	.8752	.8560	8.87	77.89
12	4	194.5[c]	−22.64	1.4353	.8754	.8562	8.91	77.80
13	3	195.0	− 0.42	1.4363	.8767	.8574	8.94	77.84
14	2	197.0[k]	14.00[j]	1.4373	Solid[n]	.8581	8.97	77.93
15	1	201.5	13.69	1.4399	Solid[o]	.8618	8.93	78.00

[a] B. p. atm. 295°, Reimer and Will, *Ber.*, 18, 2016 (1885). [b] B. p. 18 mm. 180°, König and Otten, *Ann.*, 473, 249 (1929). [c] B. p. 19 mm. 177–178°, König and Otten, *ibid.* [d] B. p. 75 mm. 210°, König and Otten, *ibid.* [e] B. p. atm. 305.9°, Gartenmeister, *Ann.*, 233, 289 (1886). [f] M. p. −9 to −12°, Gartenmeister, *ibid.* [g] d_0^0 0.8755, Gartenmeister, *ibid.* [h] M. p. 10°, Eckert and Halla, *Monatsh.*, 34, 1821 (1913). M. p. 18.5°, Le Sueur, *J. Chem. Soc.*, 87, 1898 (1905). [i] M. p. 10.5–11.5°, Nördlinger, *Ber.*, 18, 2623 (1885). M. p. 11.93°, Meyer and Reid, Ref. 4. [j] M. p. 14.01°, Meyer and Reid, *ibid.* M. p. 11°, Garner and Rushbrooke, *J. Chem. Soc.*, 1351 (1927). M. p. 12–13°, Krafft, *Ber.*, 16, 1720 (1883). [k] B. p. 15 mm. 175.5–176.5°, Krafft, *ibid.* [l] d_4^{35} 0.8541. [m] d_4^{35} 0.8497. [n] d_4^{35} 0.8503. [o] d_4^{35} 0.8541.

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(1) From a part of the Ph.D. dissertation of John R. Ruhoff, June, 1932.

(2) Kewaunee Manufacturing Company Fellow in Chemistry.

high degree of purification and to allow the determination of a wide range of physical and chemical properties.

Emphasis was placed primarily on the preparation of compounds of the highest purity consistent with the attendant experimental difficulties, rather than on high yields. Yields are therefore not reported, but in almost all reactions they were 70% or more. All distillations were carried out in precision stills.[3] Each intermediate was fractionated; except in a few instances, the portion used for synthesis boiled with a range of 0.4° or less.

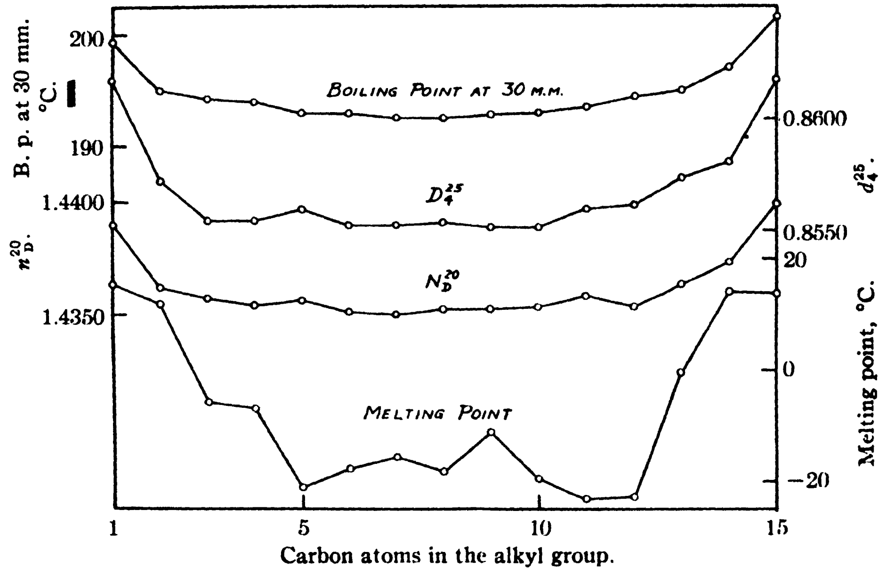

Fig. 1.

The results of the physical measurements are given in Table I and summarized in Fig. 1. When the data are plotted against the number of carbon atoms in the alcohol, the curves obtained for the boiling points, refractive indexes, and densities are very similar. Distinct alternation of the refractive indexes and densities occurs near the ends of the curves; the values for the middle five esters are practically identical. It is noteworthy that high values are found for the 5-11 and 11-5 compounds. The boiling points are remarkably close together; the extreme range is 9° and all except three of the compounds boil within 2.5° of each other. The melting points, on the other hand, cover a range of almost 40°; for the most part they show alternation.

Experimental

(A) Alcohols.—Amyl alcohol was prepared by the Grignard reaction from butyl bromide and formaldehyde. Hexyl, nonyl, undecyl, tridecyl, tetradecyl, and penta-

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(3) Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

decyl alcohols were prepared by the reduction of an ester of the corresponding acid with sodium in butyl alcohol.[4] Octyl, decyl and dodecyl alcohols were obtained by the fractionation of "Lorol," purchased from Germany. Heptyl alcohol was prepared by the reduction of heptaldehyde with iron filings in acetic acid,[5] with a small amount of nickel chloride as a catalyst. Baker 40-mesh degreased cast iron fillings were used. In over fifty reductions made in this Laboratory, the reaction has never failed to occur when nickel chloride was added.

(B) **Acids.**—Valeric, tridecylic and pentadecylic acids were prepared from the proper bromides and potassium cyanide.[6] Caproic and pelargonic acids were prepared by the malonic ester synthesis from butyl and heptyl bromides, respectively. Anhydrous butyl alcohol was used as a solvent. Caprylic, capric, lauric and myristic acids were obtained by the fractionation of the ethyl esters made from coconut oil acids. Undecylic acid was obtained by the hydrogenation of ethyl undecylenate at 220°, using a high speed stirrer[7] and 4% of nickel formate as a catalyst. Heptoic acid was prepared by the oxidation of heptaldehyde with potassium permanganate and 20% sulfuric acid at 20°.

(C) **Esters.**—**Methyl pentadecylate, ethyl myristate and propyl tridecylate** were prepared by heating together 1 mol of the acid, 4 mols of alcohol containing 3–5% of anhydrous hydrochloric acid, and 30 g. of anhydrous calcium chloride.

Butyl Laurate.—To 1 mol of lauric acid was added 3 mols of anhydrous butyl alcohol, containing 20 g. of anhydrous hydrochloric acid. After the solution had been refluxed a short time two layers formed. The lower (water) layer was removed, and the butyl alcohol distilled off slowly.

Amyl Undecylate, Hexyl Caprate, Heptyl Pelargonate, Octyl Caprylate, Nonyl Heptoate, Decyl Caproate and Undecyl Valerate.—One mol of alcohol, 1 mol plus 10 g. of acid, and 15 g. of anhydrous hydrochloric acid were warmed together until two layers were formed. The lower layer was removed, and the residue was gradually heated to 180° during the course of two hours while a slow stream of carbon dioxide was passed through it.

Dodecyl Butyrate and Tridecyl Propionate.—One mol of alcohol, 1.5 mols of acid (3 mols in the case of the propionic acid), and 25 g. of anhydrous hydrochloric acid were distilled together slowly until the boiling point rose to that of the acid.

Tetradecyl acetate was prepared from the alcohol, acetic anhydride and sodium acetate by the usual well-known procedure.

Pentadecyl Formate.—One hundred and eighty grams of pentadecyl alcohol, 460 g. of 90% formic acid and 400 cc. of carbon tetrachloride were heated in a continuous esterification apparatus for twenty-four hours; at the end of that time the reaction was 85% complete. The pentadecyl formate and the residual pentadecyl alcohol were separated and refluxed for six hours with 460 g. of anhydrous formic acid.[8] The ester layer was separated and distilled slowly with 600 cc. of carbon tetrachloride and 230 g. of anhydrous formic acid until the boiling point rose to 100°.

Purification of Esters.—The esters, with the exception of pentadecyl formate, were washed twice with warm water, then with warm 1 to 50 ammonia water, twice with warm water again, dried with calcium chloride, filtered, and distilled at 30 mm.

Freezing Points.—The freezing points were determined with a copper–constantan thermocouple in an apparatus designed by R. H. Smith, and similar to that described by Andrews, Kohman and Johnston.[9]

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(4) Meyer and Reid, THIS JOURNAL, 55, 1574 (1933).

(5) Clarke and Dreger, "Organic Syntheses," Vol. VI, p. 52.

(6) Adams and Marvel, THIS JOURNAL, 42, 312 (1920).

(7) Milligan and Reid, *Ind. Eng. Chem.*, 15, 1048 (1923).

(8) Garner, Saxton and Parker, *Am. Chem. J.*, 46, 236 (1911).

(9) Andrews, Kohman and Johnston, *J. Phys. Chem.*, 29, 914 (1925)

TABLE II

ANALYTICAL DATA ON NEW COMPOUNDS

Compound	%C	%H	Saponification value	Compound	%C	%H	Saponification value
Calcd.	74.93	12.59	256.3	Calcd.	74.93	12.59	256.3
3-13	74.81	12.66	259.3	10-6	74.85	12.43	258.1
5-11	74.94	12.46	256.7	11-5	74.92	12.69	258.2
6-10	74.88	12.59	256.3	13-3	74.94	12.51	258.8
9-7	74.91	12.61	258.0	15-1	75.10	12.65	259.5

Acknowledgment.—The authors wish to express their thanks to Messrs. Deitz and Boone for the determination of the freezing points, and to Messrs. Wenzel, Cox and Leikensohn for certain intermediates.

Summary

Fifteen isomeric esters have been prepared and their more common physical constants have been determined.

BALTIMORE, MARYLAND

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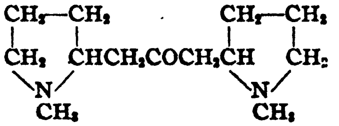
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

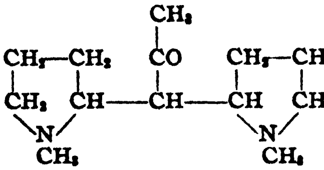
The Structure of Cuscohygrine. Synthesis of Ethyl Homohygrinate

BY W. E. SOHL AND R. L. SHRINER

Two structures have been proposed for cuscohygrine, one of the alkaloids associated with cocaine occurring in "cusco" leaves, a variety of South American coca. The structure (I) was suggested by Liebermann and Cybulski,[1] who were the first to isolate and study the alkaloid. Hess and his associates[2] have suggested the isomeric formula (II). Both structures



I



II

are in agreement with the fact that cuscohygrine gives the typical reactions for a ketone group[2a] and that oxidation with chromic acid yields hygrinic acid (III) whose structure had been established by Willstätter.[3] Although Formula I is the only one which is consistent with the formation of *n*-undecane and *n*-undecanol-6 by an exhaustive methylation and degradation[4] of dihydrocuscohygrine, the structure represented by II has been

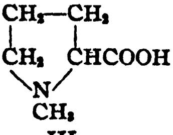
(1) Liebermann and Cybulski, *Ber.*, **28**, 578 (1895).

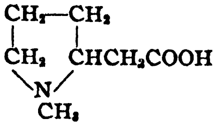
(2) (a) Hess and co-workers, *ibid.*, **53**, 781 (1920); (b) **54**, 2310 (1921); (*c*) **48**, 1986 (1915).

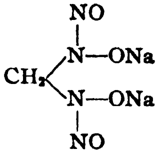
(3) Willstätter, *ibid.*, **33**, 1160 (1900).

(4) Hess and Bappert, *Ann.*, **441**, 137 (1925).

favored chiefly because the degradation of cuscohygrine by Traube's reaction[5] (nitric oxide plus sodium ethoxide) produced homohygrinic acid (IV) and the sodium salt of methylene di-isonitramine[2a] (V) which was supposed to come from the methyl ketone group of Formula (II).

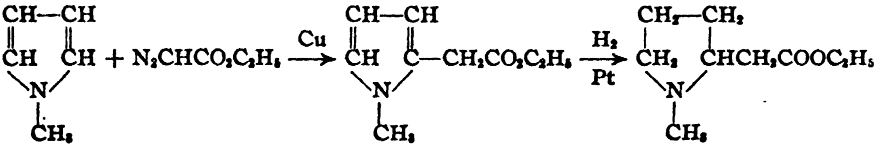

III


IV


V

Homohygrinic acid was also produced in very small amounts in the chromic acid oxidation of cuscohygrine.[6] Its structure was deduced from analyses and has not previously been confirmed by synthesis. In the present study the structure of homohygrinic acid (IV) has been definitely established by the synthesis of its ethyl ester.

All attempts to rearrange ethyl 1-pyrrylacetate resulted only in the formation of pyridine,[7] but by means of the recently described reaction[8] between 1-methylpyrrole and diazoacetic ester the 1-methyl-2-pyrrylacetic ester (I) was readily obtained. By means of a special reduction procedure this pyrrole compound was reduced catalytically to the 1-methyl-2-pyrrolidine acetic ester (II) with hydrogen and a platinum catalyst.[9]


I II

For purposes of comparison, a sample of cuscohygrine whose composition and molecular weight were checked was subjected to the Traube reaction[5] following exactly the procedure described by Hess[2a] and ethyl homohygrinate isolated. The data in Table I show the comparisons between the synthetic product and that obtained from cuscohygrine.

Although the product obtained by degradation distilled within a one-degree range it was not quite pure as evidenced by the differences in density and refractive index. Since the amount of ethyl homohygrinate obtained was about one gram it was impossible to fractionate it further in order to check the physical constants exactly. Hence, three solid derivatives were prepared and recrystallized to constant melting point. The mixed melting point determinations of all three pairs of solid derivatives

(5) Traube, *Ann.*, **300**, 81 (1898).

(6) Trier, Winterstein and Trier, "Die Alkaloide," Berlin, 1927, Vol. I, p. 242.

(7) Sohl and Shriner, THIS JOURNAL, **53**, 4168 (1931).

(8) Nenitzescu and Salomonica, *Ber.*, **64**, 1928 (1931).

(9) Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, New York, 1932, Coll. Vol. I, p. 452.

TABLE I

COMPARISON OF THE PROPERTIES OF ETHYL HOMOHYGRINATE FROM DEGRADATION AND SYNTHESIS

Property	From cuscohygrine	From synthesis	Literature
Boiling point	72–73° at 6 mm.	78° at 6 mm.	89–90°[2a] at 15 mm.
M. p. of derivatives, °C.			
(a) Methiodide	120–121	121–122	105–106[2a]
(b) Picrate	112–113	112–113	113°[2a]
(c) Chloroplatinate	Liquid	Liquid	....
(d) Chloraurate	134–135	133–134	134°[6]
Density	0.9900$^{20}_{4}$	0.9683$^{20}_{4}$	....
Refractive index	1.4501^{20}	1.4490^{20}	....

showed no depression and all analyzed correctly, thus establishing the structure of homohygrinic acid as IV.

Moreover, a study of the conditions under which ketones react with nitric oxide and sodium ethylate according to Traube's procedure demonstrated that the sodium methylene di-isonitramine (V) was produced from the ethyl alcohol used as a solvent[10] and not from cuscohygrine at all. This salt was formed from ethyl alcohol in the absence of cuscohygrine and no such precipitate was obtained when the reaction was carried out in methyl alcohol. In addition, Traube[5] showed that in ketones of the formula CH_3COCH_2R, the nitric oxide and sodium ethylate attacked the methylene group and not the methyl group. The same is true of methyl acetoacetic ester where it is the methine carbon atom which reacts.

Finally, it was established that cuscohygrine does not give the iodoform test which is characteristic of methyl ketones. In order to be certain that the tertiary amino group did not affect adversely the application of this test, the ketone $(C_2H_5)_2NCH_2CH_2COCH_3$ was synthesized and found to give a positive iodoform test. Sodium hypobromite and cuscohygrine gave no bromoform and no acetic acid; the production of which represents one other possible phase of the haloform reaction.[11]

Two remaining objections to Formula I have been cited. It is stated that such a compound should condense with benzaldehyde whereas no such reaction seems to take place. Although diethyl ketone does condense with benzaldehyde[12] the methyl ketones generally react much more readily[13] and hence the non-reactivity of cuscohygrine with benzaldehyde really counts as evidence against formula II.

Treatment of cuscohygrine with bromine yielded a red compound containing three atoms of bromine. This derivative, which may be a mono-

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(10) Stechow [*Ber.*, **57**, 1615 (1924)] has also pointed out that ethyl alcohol, nitric oxide and sodium ethylate produce sodium methylene di-isonitramine and that conclusions regarding structure cannot be drawn from this phase of the Traube reaction.

(11) Woodward and Fuson, THIS JOURNAL, **55**, 3472 (1933).

(12) Vorländer, *Ann.*, **294**, 296 (1897).

(13) Claisen, *Ber.*, **14**, 2471 (1881); Harries and Müller, *ibid.*, **35**, 968 (1902); Harries and Bromberger, *ibid.*, **35**, 3089 (1902).

bromo-dihydrobromide or a perbromide, liberated iodine from potassium iodide and on treatment with acetone produced bromoacetone and regenerated cuscohygrine as its dihydrobromide salt.

The last objection cited against formula (I) is that it does not explain the formation of two isomeric hydrazones. It should be pointed out that there are two similar asymmetric carbon atoms and hence the two reported hydrazones may be derived from the meso and racemic forms of (I), respectively.

Experimental

Ethyl 1-Methyl-2-pyrrylacetate.—In a flask equipped with dropping funnel and reflux condenser was placed 70 g. of 1-methylpyrrole with 2 g. of fine copper bronze. The liquid was warmed on the steam cone and 35 g. of ethyl diazoacetate was added during one hour and heated for an additional half hour. The copper was removed by filtration and the liquid fractionated. Fifty grams of 1-methylpyrrole was recovered and 24.7 g. (67.3%) of 1-methyl-2-pyrrylacetic ester was obtained as a light yellow liquid boiling at 115–118° (10 mm.) and 105–110° (6 mm.).

Reduction of Ethyl 1-Methyl-2-pyrrylacetate.—The reduction was carried out in a special vessel made by joining the neck of a 200-cc. round-bottomed flask through a 5-mm. Pyrex glass stopcock to the bottom of a second 200-cc. round-bottomed flask. This arrangement permitted the catalyst (0.6 g. platinum oxide) to be reduced separately and the ester (7.5 g.) could be introduced and the apparatus freed from air. Additional catalyst could be added as needed.

After the reduction was completed (twenty-four hours) the catalyst was removed by filtration and 15 cc. of concentrated hydrochloric acid added to the filtrate. The alchol and acetic acid were removed by distillation under vacuum. The residue was then treated with cold saturated potassium carbonate solution, extracted with ether and dried over solid potassium carbonate. The ether was then evaporated and the ester fractionated; b. p. 88–89° (10 mm.), 78° (6 mm.); d_4^{20} 0.96838; n_D^{20} 1.4465; M_D calcd., 47.35; found, 47.30.

Anal. Calcd. for $C_9H_{17}O_2N$: N, 8.18. Found: N, 8.33.

Cuscohygrine.—Thirty-five grams of cuscohygrine dinitrate was dissolved in 25 cc. of water and an excess of saturated sodium hydroxide solution added. The free base separated as a clear oil. The aqueous lower layer was extracted five times with ether. The extracts were combined and dried over anhydrous magnesium sulfate for several days. The ether solution was then filtered and the ether distilled.

The cuscohygrine was distilled at 2 mm. pressure and boiled at 118–125° (corr.); d_4^{20} 0.9733; n_D^{20} 1.4832; M_D calcd., 66.02; found, 65.75. *Mol. wt.* (cryoscopic in benzene). Calcd. for $C_{13}H_{24}ON_2$: 224. Found: 223.

Anal. Calcd.: N, 12.50. Found: N, 12.27.

Cuscohygrine gave no iodoform when treated with sodium hypoiodite and no bromoform with sodium hypobromite as the reagent. A careful examination of the products of the latter reaction showed that no acetic acid was produced.[11]

No condensation products with benzaldehyde could be obtained in the presence of either alkali or acid using the customary procedures.[12,13]

Preparation of Ethyl Ester of Homohygric Acid from Cuscohygrine.—A three-necked, one-liter flask equipped with a mercury-sealed stirrer, a dropping funnel and a tube for entrance of nitric oxide gas was swept free of air with nitric oxide which was generated in a Kipp apparatus by the action of dilute (1:1) nitric acid on copper. The nitric oxide was washed with water to remove higher oxides of nitrogen and then dried in a tube filled with soda lime. When the brown color due to the presence of higher oxides of nitrogen disappeared the flask was considered to contain no air.

Six-tenths mole of sodium was dissolved in 250 cc. of absolute alcohol and then run into the nitric oxide filled flask. The cuscohygrine was added and stirring started. The nitric oxide was absorbed very rapidly at first and then at about 15 cc. per minute. After eighteen hours the absorption had ceased. About 30 cc. of water was added to the cherry-red solution which caused a slimy solid to precipitate. This solid was filtered, dissolved in 100 cc. of water and the solution acidified with acetic acid. Addition of lead acetate gave a precipitate which on decomposition with sulfuric acid gave lead sulfate. No pure organic compound could be isolated from this solution.

The alcoholic filtrate from which the slimy precipitate was removed was next acidified with hydrochloric acid and filtered. The alcohol was evaporated and the residual solution was made alkaline with sodium hydroxide and extracted six times with ether to remove unchanged cuscohygrine which amounted to 5 g.

The alkaline residue was acidified with hydrochloric acid and evaporated to dryness over water-bath, then dried completely in a vacuum over phosphorus pentoxide. The brown hard residue was broken up and placed in a 500-cc. round-bottomed flask with 250 cc. of absolute alcohol and the mixture saturated with dry hydrogen chloride. This mixture was refluxed for one day, then cooled to below 0° in an ice–salt-bath and made alkaline with saturated solution of potassium carbonate. The alcohol ester layer was separated and dried with magnesium sulfate. The alcohol was distilled and a high boiling fraction collected. This high boiling material was next refractionated and the portion boiling at 72–73° (6–7 mm.) collected. This amounted to about 1 g., n^{20}_{D} 1.4501; d^{20}_{4} 0.9900.

Anal. Calcd. for $C_9H_{17}O_2N$: N, 8.18; C, 63.10; H, 10.02. Found: N, 10.27, 10.24; C, 62.75; H, 10.24.

These analyses show that the degradation product was not pure but the amount available was insufficient for further fractionation.

Preparation of Derivatives.—Three solid derivatives of the synthetic ester and of the ethyl homohygrinate from cuscohygrine were prepared. Their properties and analyses are summarized in Table II.

Table II

Derivatives of Ethyl 1-Methyl-2-pyrrolidineacetate

		Synthetic			From cusocohygrine		
			Analysis, %			Analysis, %	
	Formula	M. p., °C.	Calcd.	Found	M. p., °C.	Calcd.	Found
Picrate	$C_{15}H_{20}O_9N_4$	112–113	N, 14.00	14.58	112–113	N, 14.00	14.27
Methiodide	$C_{10}H_{20}O_2NI$	121–122	I, 40.54	40.46	120–121	I, 40.54	40.89
Chloraurate	$C_9H_{17}O_2N \cdot AuCl_3 \cdot 2H_2O$	133–134	Au, 38.61	38.40	134–135	Au, 38.61	38.90

The chloroplatinate and methyl *p*-toluene sulfonate were liquids and the flavianic acid salts were too soluble.

Action of Bromine on Cuscohygrine.—The free base was dissolved in 90 g. of glacial acetic acid and 10 g. of acetic anhydride and treated with 6.4 g. of bromine whereupon an oily red precipitate formed which later solidified. This was removed by filtration. The product could not be recrystallized and hence the analysis for bromine was high.

Anal. Calcd. for $C_{13}H_{25}N_2OBr_3$: Br, 51.56. Found: Br, 53.37.

The red substance on treatment with acetone precipitated a white powder melting at 236° with decomposition at 240°.

Anal. Calcd. for $C_{13}H_{26}N_2OBr_2$: Br, 41.40. Found: Br, 40.70.

A sample of cuscohygrine dihydrobromide was prepared from cuscohygrine and hydrobromic acid. It melted at 239° and was identical with the above product.

1-Diethylaminobutanone-3.[14]—In a 500-cc. flask fitted with a reflux condenser was placed 43 g. of formalin solution, 54.7 g. of diethylamine hydrochloride and 145 g. of acetone. The mixture was refluxed for twelve hours and the acetone and some water removed by distillation. The residue was treated with potassium carbonate solution and extracted with ether. The ether extract was dried over potassium carbonate and then fractionated. The amino ketone boiled at 84° (30 mm.) and 53° (4 mm.); yield, 31 g. or 42%.

Anal. Calcd. for $C_8H_{17}ON$: N, 9.79. Found: N, 9.80.

Treatment of this amino ketone with sodium hypoiodite yielded yellow crystals of iodoform melting at 118–119°.

Summary

1. Ethyl 1-methyl-2-pyrrolidineacetate has been synthesized by the catalytic reduction of the ethyl 1-methyl-2-pyrrylacetate which was prepared from 1-methylpyrrole and ethyl diazoacetate.

2. This synthetic ester was identical with ethyl homohygrinate obtained as a degradation product of cuscohygrine by the action of nitric oxide and sodium ethylate.

3. Cuscohygrine did not react with benzaldehyde and failed to give an iodoform test.

4. These data together with previous investigations indicate that cuscohygrine is probably a *sym-bis*-(1-methylpyrrolidyl)-acetone.

[14] Mannich, *Arch. Pharm.*, **255**, 261 (1917).

URBANA, ILLINOIS

RECEIVED MAY 29, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI]

Synthesis and Resolution of Phenyl-α-(β-methoxynaphthyl)-aminomethane

BY FRANCIS EARL RAY AND WILLIAM A. MOOMAW

In a previous paper[1] the authors described the effect of negative substituents in the benzene ring on the amines resulting from the condensation of aromatic aldehydes with β-naphthol and ammonia. It was found that the presence of negative substituents decreased the stability of the amines.

As it was thought that the tautomerism of the β-naphthol contributed to the instability of the amine we sought to replace the ionizable hydrogen with a methyl group.

When, however, β-methoxynaphthalene was mixed with benzaldehyde and ammonia no reaction took place. It was necessary, therefore, to use other means to synthesize the desired amine. Attempts to methylate or acetylate the hydroxy group, I, were unsuccessful as the amino group reacted first.[2] If the amino group was first blocked the hydroxyl group could be methylated or acetylated but it was then impossible to remove the amino acetyl group without decomposing the compound.

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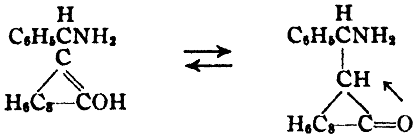
[1] Ray and Moomaw, THIS JOURNAL, **55**, 749 (1933).

[2] Nzeer Ahmed, Master's Thesis, University of Cincinnati, 1933



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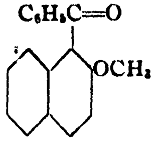
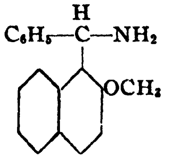


III

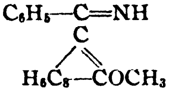
An attempt was made to prepare the desired amine by first making the ketone, III, by the Friedel–Crafts reaction, converting this into the oxime, and finally reducing the oxime to the amine, IV.

The ketone, III, was readily prepared but it did not react with hydroxylamine or phenylhydrazine. This is an extension of Meyer's rule[3] to the effect that when a carbonyl group is connected to an aromatic nucleus which contains two substituents ortho to it no oxime or hydrazone is formed. In view of the fact that the phenylhydrazone was prepared by indirect means it may also be possible to find conditions that will give the desired oxime. The problem of steric hindrance as applied to these compounds is being studied further in this Laboratory.

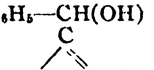
There was also the possibility that the methyl group might, under the influence of aluminum chloride, migrate from oxygen to a carbon of the nucleus, a somewhat general reaction of the phenol ethers.[4]



IV



V



m. p. 98°

VI

In order to determine if the compound from the Friedel–Crafts condensation had the structure III, we sought to prepare it by means of the Grignard reaction. β-Methoxynaphthyl-α-magnesium iodide was treated with benzonitrile. On hydrolysis with water and dilute acid a compound was obtained that contained iodine. When this compound was treated with alkali an iodine-free basic substance was obtained which was identified as phenyl-α-(β-methoxynaphthyl)-ketimine, V. Hot alkali or boiling acid hydrolyzed this to the ketone, III, identical with that prepared by the Friedel–Crafts reaction. Each was separately reduced to the identical alcohol,[5] VI, thus proving that no rearrangement had occurred in the reaction with aluminum chloride. The same alcohol was obtained by reaction of β-methoxynaphthyl-α-magnesium iodide with benzaldehyde. When the Grignard reagent was treated with methyl benzoate there was isolated in addition to the ketone, III, the tertiary alcohol, VII.

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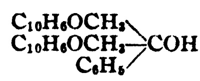
[3] Meyer, *Ber.*, **29**, 830 (1896); compare the esterification rule of Meyer and Sudborough, *ibid.*, **27**, 510, 1580, 3146 (1894).

[4] Smith, This Journal, **55**, 849 (1933).

[5] Bauer [*Ber.*, **42**, 2589 (1909)] has reported a melting point of 237° for this compound but gives no analytical data. This melting point is entirely out of line with that of similar compounds; diphenylcarbinol 68°, α-naphthylphenylcarbinol 86°, di-α-naphthylcarbinol 147°.



$$\begin{array}{l} C_{10}H_6OCH_3 \searrow \\ C_{10}H_6OCH_3 \rightarrow COH \\ C_6H_5 \nearrow \end{array}$$

VII

It is interesting to note that although the ketone gave no hydrazone the ketimine, V, readily reacted with phenylhydrazine to give the required phenylhydrazone, VIII.

$$\underset{\text{V}}{C_6H_5(C_{10}H_6OCH_3)C{=}\boxed{NH \quad H_2}NNHC_6H_5} \longrightarrow \underset{\text{VIII}}{C_6H_5(C_{10}H_6OCH_3)C{=}NNHC_6H_5}$$

Though we were unable to use the ketone in the preparation of the amine due to our inability to prepare the intermediate oxime, our objective was reached by reducing the ketimine, V, to the amine, IV, with sodium amalgam. This amine was resolved into its enantiomorphous forms by means of *l*-malic acid.

The new amine showed none of the tendency to decompose that had been noted for the amines with a free naphtholic group; the specific rotation was over three times as great; and the compound was more basic.

Phenyl-β-naphtholaminomethane may be recrystallized from acetone but our amine reacts with acetone at ordinary temperatures giving a sparingly soluble Schiff base that is excellent for purposes of identification. Benzaldehyde also reacts with our amine to give a similar Schiff base.

Experimental Part

Phenyl-α-(β-methoxynaphthyl) Ketone.—This compound was prepared by condensing benzoyl chloride and β-methoxynaphthalene by means of aluminum chloride in carbon disulfide. After reacting, the mass was poured into water and steam distilled. The residue was recrystallized from alcohol; m. p. 125° corr.; yield 85%.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.44; H, 5.34. Found: C, 82.6; H, 5.4. *Mol. wt.* (Rast method) Calcd.: 262. Found: 270.

α-Iodo-β-naphthol, m. p. 94°, was prepared in 72% yields according to the method of Mendola.[6]

α-Iodo-β-methoxynaphthalene.—This was obtained from the above-mentioned compound by treatment with methyl sulfate and 10% alkali. One recrystallization from alcohol gave cream colored plates melting at 88°. The yield was 80%.

Anal. Calcd. for $C_{11}H_9OI$: C, 46.49; H, 3.17. Found: C, 46.8; H, 3.2.

β-Methoxynaphthyl-α-magnesium Iodide.—This Grignard reagent was prepared by using the magnesium iodide catalyst prepared according to Gilman's[7] method. The concentration was determined by titration and a conversion as high as 80% was obtained.

Phenyl-α-(β-methoxynaphthyl)-carbinol.—The Grignard reagent prepared as described was treated with redistilled benzaldehyde. On decomposition of the addition product the alcohol was obtained. Recrystallization from alcohol in which it was rather soluble gave the pure compound melting at 98° corr.; yield 70%.

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(6) Mendola, *J. Chem. Soc.*, **47**, 526 (1885).

(7) Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1927).

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.5; H, 6.0. *Mol. wt.* (Rast method) Calcd. 264. Found: 265.

This alcohol was also obtained by reducing the ketone prepared by the Friedel–Crafts reaction with sodium amalgam. Mixed melting points showed them to be identical.

Phenyl-α-(β-methoxynaphthyl)-ketimine Hydriodide.—Twenty grams of α-iodo-β-methoxynaphthalene was converted into the Grignard reagent and filtered from the undissolved magnesium. Six grams (0.87 mol) of pure benzonitrile in 25 cc. of ether was slowly added. The addition product first settled as an oil but after refluxing for four hours it changed to a yellow crystalline solid. The ether was decanted and the residue was treated with ice and dilute sulfuric acid. At first the product of hydrolysis separated as an oil but soon solidified to a yellow crystalline mass. When recrystallized from hot water it melted at 180° corr. An alcoholic solution when treated with silver nitrate gave a precipitate of silver iodide. The iodide is soluble in alcohol, benzene, acetone and chloroform as well as hot water. It is sparingly soluble in ether and cold water; yield 90% based on the Grignard concentration.

Anal. Calcd. for $C_{18}H_{16}ONI$: C, 55.53; H, 4.14; I, 32.79. Found: C, 55.7; H, 4.2; I, 33.0.

The ketimine hydroiodide was remarkably stable. Boiling with dilute hydrochloric acid for two hours resulted in only a 25% hydrolysis to the ketone. This product melted at 125° and was identical with the ketone prepared by methods already described.

Phenyl-α-(β-methoxynaphthyl)-ketimine was prepared from the hydroiodide by neutralizing in ice-cold alcoholic solution with an equal volume of dilute potassium hydroxide. After standing some hours a coarse granular precipitate of the free ketimine separated. An almost quantitative yield of the base resulted, melting at 98–99°. The free ketimine was very soluble in alcohol, ether and benzene, but was only sparingly soluble in water and petroleum ether. It dissolved in dilute mineral acids on warming with the formation of salts similar to the hydroiodide.

Anal. Calcd. for $C_{18}H_{15}ON$: C, 82.78; H, 5.75; N, 5.36. Found: C, 82.5; H, 5.8; N, 5.4.

The phenylhydrazone could not be prepared directly from the ketone. It was, however, obtained by warming 0.7 g. of the ketimine in 10 cc. of alcohol with 0.5 g. of phenylhydrazine and one cc. of glacial acetic acid. Two cc. of water was added and the mixture allowed to stand. After six hours one gram of material (80% of theoretical) had settled out. It was washed with alcohol and melted at 183.5° corr.

Anal. Calcd. for $C_{24}H_{20}ON_2$: C, 81.82; H, 5.72; N, 7.95. Found: C, 81.6; H, 5.7; N, 8.35.

Phenyl-di-α-(β-methoxynaphthyl)-carbinol.—The reaction between the Grignard reagent and methyl benzoate gave largely the ketone melting at 125°, which was extracted from the reaction mass with hot alcohol. The residue proved to be the tertiary alcohol. It was recrystallized from nitrobenzene, washed with hot alcohol and found to melt at 202–203° corr.

Anal. Calcd. for $C_{29}H_{24}O_3$: C, 82.82; H, 5.76. Found: C, 82.1; H, 5.8. *Mol. wt.* Calcd. 420. Found: 426.

Phenyl-α-(β-methoxynaphthyl)-aminomethane.—The ketimine was reduced to the amine by the following method. To 100 g. of 2% sodium amalgam was added 40 cc. of dry benzene, 20 cc. of dry ether and 15 cc. of absolute alcohol. To this was added in small portions 8.5 g. of the ketimine. The flask was shaken after each addition. When the ketimine had been added the flask was shaken at five-minute intervals for twenty-five minutes. The organic liquid was decanted, dried with sodium sulfate and evaporated to dryness. This residue was well washed with petroleum ether to remove the coloring matter and twice recrystallized from alcohol. It then melted at 102° corr.; yield 70%. The amine was readily soluble in cold benzene and hot alcohol and moderately soluble in cold alcohol, ether and chloroform.

Anal. Calcd. for $C_{18}H_{17}ON$: C, 82.13; H, 6.46; N, 5.32. Found: C, 82.0; H, 6.6; N, 5.6.

Schiff Base with Acetone.—One-half gram of the amine was dissolved in 5 cc. of alcohol. Two cc. of acetone was added and the mixture heated to boiling. After standing one and one-half hours 0.47 g. of material separated. The crystals were washed with alcohol; m. p. 162° corr.

Anal. Calcd. for $C_{21}H_{21}ON$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.5; H, 7.2; N, 4.97.

Schiff Base with Benzaldehyde.—Seven-tenths gram of the amine was dissolved in 8 cc. of hot alcohol. Five-tenths gram of benzaldehyde was added and the solution allowed to stand. After two hours an oil separated which was removed and rubbed with a few drops of alcohol to induce crystallization. The crystals were washed with alcohol. A yield of 0.73 g. melting at 98° corr. was obtained.

Anal. Calcd. for $C_{25}H_{21}ON$: C, 85.43; H, 6.03; N, 3.99. Found: C, 85.7; H, 6.3; N, 4.0.

N-Acetyl-phenyl-α-(β-methoxynaphthyl)-aminomethane.—One gram of the amine was dissolved in 10 cc. of benzene and 3 cc. of ether. An excess (0.5 cc.) of acetyl chloride was added and the mixture treated with pyridine. One-half gram melting at 186.5–187° was obtained. By mixed melting points this was shown to be the same as the compound obtained by first acetylating and then methylating phenyl-β-naphthol-aminomethane.[3]

Anal. Calcd. for $C_{20}H_{19}O_2N$: N, 4.59. Found: N, 4.7.

Phenyl-α-(β-methoxynaphthyl)-aminomethane Hydrochloride.—This compound was prepared by treating an alcoholic solution of the amine with dilute hydrochloric acid. It melted with decomposition at 237–240°.

Anal. Calcd. for $C_{18}H_{18}ONCl$: Cl, 11.84. Found: Cl, 12.0.

Resolution of the Amine.—One mol (2.53 g.) of the amine was dissolved in 60 cc. of alcohol at 40°. To this was added 1.27 g. (one mol) of *l*-malic acid in 10 cc. of alcohol. Crystals soon appeared and after standing for four hours they were filtered and washed with alcohol. A yield of 1.81 g. of the salt melting at 186° was obtained. Three more fractions were obtained from the mother liquor, the next to the last being the purest which melted at 164°. When dissolved in methyl alcohol the salts showed but slight optical activity.

The salts were treated with potassium hydroxide and extracted with ether. The first fraction showed the highest dextro rotation and gave α_D +3.05°, $[\alpha]_D^{25}$ +197°, for 0.1550 g. of amine in 10 cc. of ether in a 1-dm. tube.

The third fraction contained the levo rotatory amine and 0.1229 g. of the free base in 10 cc. of ether gave α_D −2.49°, $[\alpha]_D^{25}$ −202°.

As yet neither of the active forms of the amine has been obtained in a crystalline state. When small amounts of *d*- and *l*-amines were mixed they at once solidified to give the racemic compound.

Summary

Phenyl-α-(β-methoxynaphthyl)-aminomethane has been prepared and resolved into its optical antipodes. Many of the derivatives have also been prepared.

This amine is quite stable in contrast to phenyl-β-naphtholaminomethane. This lends weight to the theory that the tautomerism of the hydroxyl group in the latter compound contributes to its instability.

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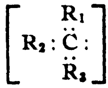
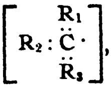
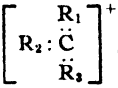
[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Spatial Configuration of the Valences in Tricovalent Carbon Compounds[1]

BY EVERETT S. WALLIS AND FREDERIC H. ADAMS

The tetrahedral configuration of the valences of quadricovalent carbon has been generally accepted since the classical researches of van't Hoff and Le Bel. However, the spatial arrangement of the groups in compounds containing a tricovalent carbon atom has not been definitely proved. For the sake of clearness in discussion all tricovalent carbon compounds may be divided into three classes: (1) "carbanions"[2]  $\left[\begin{matrix} & R_1 & \\ R_2 : & \ddot{\underset{\cdot\cdot}{C}} & : \\ & R_3 & \end{matrix}\right]^-$, (2) free radicals  $\left[\begin{matrix} & R_1 & \\ R_2 : & \ddot{\underset{\cdot\cdot}{C}} & \cdot \\ & R_3 & \end{matrix}\right]$, and (3) carbonium ions  $\left[\begin{matrix} & R_1 & \\ R_2 : & \ddot{\underset{\cdot\cdot}{C}} & \\ & R_3 & \end{matrix}\right]^+$. Much interest is attached to the possibility of the existence of a non-planar configuration in these compounds. If such a spatial arrangement be true, asymmetry would be possible when the three aryl groups around the central carbon atom are different. A study of the behavior of such compounds toward polarized light would also enable us to determine the degree of stability of the antimeric configurations. It is hardly possible experimentally to resolve such substances directly into *dextro* and *levo* forms. It would be necessary to prepare the corresponding quadricovalent compound in its enantiomorphic modifications, and then to determine whether the rotatory power of such compounds is retained or lost upon transition into the tricovalent state, and return to the quadricovalent condition. If optical activity of the final product is retained, it would necessarily imply that the tricovalent molecule from which it was formed was also optically active. An asymmetric spatial configuration would therefore be experimentally demonstrated. If, however, on assuming the tricovalent state the substituted groups move into the plane of the central carbon atom, or acquire any other arrangement[3] which prevents the maintenance of asymmetry, then enantiomorphic modifications cannot exist and the preparation of these substances in optically active form is impossible. Previous attempts by several investigators[4] to settle this question failed because they were unable to obtain the necessary starting materials in optically active form. However, the resolution[5] of phenylbiphenyl-α-naphthylmethylthioglycolic acid has made it possible to obtain the optically active triarylmethane derivatives which are necessary for this polarimetric investigation.

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(1) This paper is based upon a thesis submitted by Frederic H. Adams to the Faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Communicated in the form of two papers to the Division of Organic Chemistry at the 83rd and 85th meetings of the American Chemical Society held at New Orleans, La., March 28 to April 1, 1932, and at Washington, D. C., March 26 to 31, 1933, respectively.

(2) The above word is here proposed for a negatively charged carbon ion in contrast to the term "carbonium," which indicates a positively charged ion.

It was the aim of these investigations to test more thoroughly this method of resolution, to prepare if possible other asymmetric carbinols in their optically active modifications, and to study the behavior of these compounds and their derivatives toward polarized light when they are made to undergo chemical change to the tricovalent state. Furthermore, a study has been made of the optical stability of certain asymmetric groups during reactions in which they apparently go through the free radical stage, notably in the Kolbe synthesis by electrolysis of the potassium salts of fatty acids, and in the Wurtz reaction.

Attention was first directed toward the resolution of aliphatic and mixed aliphatic–aromatic carbinols by means of their thioglycolic acid derivatives. In all cases these were unsuccessful. One illustration follows.

Methylethylphenylcarbinol was converted into its chloride, and the latter compound was made to react with thioglycolic acid according to the equation

$$(CH_3)(C_2H_5)(C_6H_5)CCl + HSCH_2COOH \longrightarrow \underset{\text{(I)}}{(CH_3)(C_2H_5)(C_6H_5)CSCH_2COOH} + HCl$$

The resulting compound (I), m. p. 137–138°, was found to combine with brucine and other alkaloids, but such salts showed a tendency to decompose into unsaturated hydrocarbons and alkaloid thioglycolates. No resolution was effected.

Investigations were therefore directed to the further applicability of this method of resolution to methane derivatives of the true aryl type. In such compounds decomposition reactions of the above type would be avoided. It was also thought to be of scientific interest to resolve if possible a triarylmethane derivative in which two of the aryl groups are bound together to form a heterocyclic ring. A comparison of the spatial stability of such a compound with that of phenylbiphenyl-α-naphthylmethylthioglycolic acid, in which the substituents are simple aryl groups, might give us an indication of the strain set up in the molecule by the "internuclear" bridge, and also the amount of distortion from the normal tetrahedral grouping.

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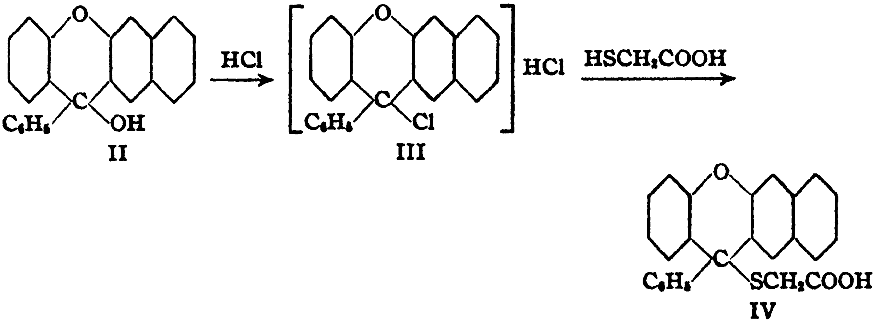
[3] Researches of this kind are well suited to clarify the question of the benzenoid or quinonoid constitution of these tricovalent compounds when they contain aryl groups. The question whether such substances can assume the quinonoid state and at the same time maintain an asymmetric configuration has previously been discussed [Wallis, THIS JOURNAL, **53**, 2253 (1931)].

[4] Schmidlin and Garcia-Banûs, *Ber.*, **45**, 3188 (1912); Meisenheimer and Neresheimer, *Ann.*, **423**, 105 (1921); Karagunis, Ph.D. Dissertation, Freiburg, 1926; H. Krauss, Ph.D. Dissertation, Munich, 1927.

[5] (a) Wallis, *Proc. Nat. Acad. Sci.*, **16**, 215 (1930); (b) Wallis, THIS JOURNAL, **53**, 2253 (1931); (c) **54**, 1693 (1932).

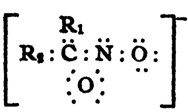
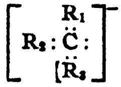
Accordingly 12-phenyl-12-β-benzoxanthenol (II) was prepared and converted into its orange-red chloride–hydrochloride (III) according to the method of Gomberg and Schoepfle.[6] The latter compound in benzene solution reacted with thioglycolic acid to give a good yield of 12-phenyl-12-β-benzoxanthenethioglycolic acid (IV), a colorless crystalline solid melting at 187–188°.



Resolution of this acid by fractional crystallization of its brucine salt gave a *levo* modification $[\alpha]^{20}_{D}$ −48.5° in acetone. From the mother liquors were obtained samples of mixed *dextro* acid of varying rotations up to $[\alpha]^{20}_{D}$ +28.9°.

This compound (IV) was found to be much more easily racemized than phenylbiphenyl-α-naphthylmethylthioglycolic acid.

It was also found to turn orange slowly when exposed to diffuse light and rapidly when exposed to sunlight. Mineral acids, such as concentrated hydrochloric acid or sulfuric acid, dissolve it with the formation of deep orange-colored solutions. In fact this color was observed when any compound containing the 12-phenyl-β-benzoxanthenyl radical was treated with concentrated mineral acid. These reactions were always accompanied by racemization.

The Spatial Configuration of the Valences in Tricovalent Carbanions.—The work of Kuhn and Albrecht, and of Shriner and Young[7] on the sodium salts of optically active secondary nitroparaffins has shown that in all probability optically active anions of the type $\left[R_2:\overset{R_1}{\underset{\cdot\cdot}{C}}:NO_2\right]^-$ are capable of existence. It must be pointed out, however, that the alternative formula for such ions,  $\left[\begin{matrix} & R_1 & & \\ R_2: & \ddot{C} & :\ddot{N}: & \ddot{O}: \\ & :\ddot{O}: & & \end{matrix}\right]^-$, has not yet been definitely disproved. A study of the spatial configuration of an anion of the type  $\left[\begin{matrix} & R_1 \\ R_2: & \ddot{C}: \\ & R_3 \end{matrix}\right]^-$ in which R_1, R_2 and R_3 are different aryl groups should therefore be of interest, for in this case no such alternative formula is likely, and the presence of optical activity can only be explained by the asymmetric non-planar arrangement of the three substituent groups and the electron pair.

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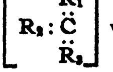
[6] Gomberg and Schoepfle, This Journal, 39, 1652 (1917).

[7] Kuhn and Albrecht, *Ber.*, 60, 1297 (1927); Shriner and Young, This Journal, 52, 3332 (1930).

The salt-like nature of the sodium compounds of triphenylmethyl and its analogs in ether solution has been demonstrated by Schlenk and Marcus.[8] Kraus and his co-workers[9] have prepared these organo-metallic compounds by the action of sodium on triarylchloromethanes in liquid ammonia, and have shown by conductivity measurements that the C–Na bond in this solvent is ionic and not covalent.

As has been noted,[10] *l*-12-phenyl-12-β-benzoxanthenethioglycolic acid (IV) has been subjected to the action of sodium in liquid ammonia in the absence of oxygen. The deep orange-brown sodium triarylmethyl so formed was then treated with a slight excess of dry ammonium bromide. The solution was immediately decolorized, and the colorless methane derivative, 12-phenyl-β-benzoxanthene, precipitated out. This material was found to be free from sulfur and optically active; in one experiment it exhibited $[\alpha]^{20}_{D}$ −11.7° in acetone solution. From these data it is evident that a triarylmethyl anion can exist in the optically active state for an appreciable length of time, and that its three covalence bonds are not coplanar with the central carbon atom.

The Spatial Configuration of the Valences in Tricovalent Carbonium Ions.—It is a well-known fact that an atom attached to an asymmetric carbon atom can be replaced by another atom without occurrence of complete racemization. In many of these reactions it would appear that the replacement involves an exchange of anions, and that two electrons are withdrawn from the octet of the asymmetric carbon atom. This interpretation involves the momentary existence of a carbonium ion,  $\left[\begin{matrix} & R_1 \\ R_2: & \ddot{C} \\ & R_3 \end{matrix}\right]^+$ which is sufficiently stable to maintain an asymmetric configuration. Several investigators[11] have made use of this concept to explain their experimental results. However, there are recorded facts which indicate that in the absence of a special mechanism which leads to Walden

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(8) Schlenk and Marcus, *Ber.*, 47, 1664 (1914).

(9) Kraus and Kawamura, THIS JOURNAL, 45, 2756 (1923); Kraus and Rosen, *ibid.*, 47, 2739 (1925).

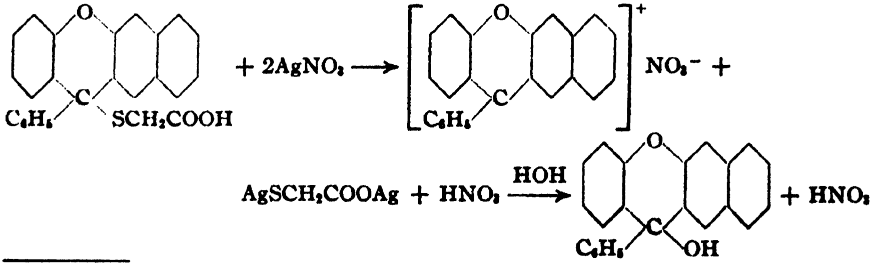
(10) Adams and Wallis, *ibid.*, 54, 4753 (1932).

(11) Billmann, *Ann.*, 388, 330 (1912); McKenzie and Clough, *J. Chem. Soc.*, 103, 687 (1913); Jones and Wallis, THIS JOURNAL, 48, 169 (1926).

inversion such a carbonium ion is optically unstable. In a study of certain spontaneous migrations of optically active groups from oxygen to sulfur, Kenyon and Phillips[12] have shown that the rearrangement is accompanied by racemization.

In the light of these experiments it therefore seemed important to investigate the problem further. There are many reactions which indicate that triarylmethyl radicals exist as carbonium ions. The physical and chemical properties of solutions of triarylmethyl halides in liquid sulfur dioxide may be cited as an example. Many investigators[13] also believe that such ions are present in the halochromic compounds of triarylmethyl derivatives with inorganic acids and salts. In a recent publication[5b] from this Laboratory this question has been discussed, and experimental facts were submitted which have a direct bearing on the constitution of these compounds. The triarylmethyl derivatives also undergo many reactions which involve substitution on the methane carbon atom. These reactions would imply an exchange of anions and the momentary withdrawal of two electrons from the octet of the central carbon atom. The present investigations include a study of such replacements when the central carbon atom is asymmetric. If the substitution is accompanied by racemization it would appear that not even momentarily can a triarylmethyl positive radical maintain its asymmetry in the absence of a special mechanism which leads to Walden inversion. On the other hand, if optical activity persists after such transformations one must conclude that such positive groups for a certain length of time are able to keep their covalent linkages non-planar with the central carbon atom, and do not "oscillate between the two forms of opposite configuration."

Two optically active triarylmethane derivatives were used for this purpose, *d*- and *l*-12-phenyl-12-β-benzoxanthenethioglycolic acid (IV) and *d*- and *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid (V). Many of our experiments gave results which seemed to support the first conclusion. When compound (IV) was dissolved in acetone containing small amounts of water, and treated in the cold with an aqueous solution of silver nitrate, the $-SCH_2COOH$ group was replaced by $-OH$. In all cases, however, the carbinol so formed was inactive. The reaction may be formulated as


O
C
C_6H_5
SCH_2COOH
$+ 2AgNO_3 \longrightarrow$
O
C
C_6H_5
+
NO_3^- +
$AgSCH_2COOAg + HNO_3 \xrightarrow{HOH}$
O
C
C_6H_5
OH
$+ HNO_3$

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(12) Kenyon and Phillips, *J. Chem. Soc.*, 1676 (1930).

(13) Baeyer and Villiger, *Ber.*, **35**, 1189, 3013 (1902); Hantzsch, *ibid.*, **54**, 2573, 2613 (1921); **63B**, 1181 (1930); Dilthey, *J. prakt. Chem.*, [2] **109**, 273 (1925); **118**, 321 (1928); **124**, 81 (1929).

If the reaction was carried out in ethyl alcohol solution, the corresponding ethyl ether was produced. This compound also showed no appreciable rotation. Certain experiments with (V) gave similar results. Replacement of the $-SCH_2COOH$ group by the action of halogens or thionyl chloride gave in every instance an inactive triarylmethyl halide.

However, certain observations[14] have been made which might indicate that a positive radical of the above type under certain conditions can maintain an asymmetric configuration. When compound (V) was treated with silver nitrate under the same conditions as were used in our experiments with compound (IV), optically active products were obtained. It is to be noted that in the case of the carbinols the replacement was accompanied by a change in the sign of the rotatory power. This, however, did not take place when the corresponding optically active ethyl ethers were produced.

If we compare these results with those obtained with compound (IV) it would appear that the stability of the group is somewhat dependent upon the nature of the substituents present. If the molecule is of such a nature that distortion of the valences around the central carbon atom is pronounced, as is most certainly the case in molecules of the above type containing an internuclear oxygen bridge, then such a radical, even though it exists but momentarily, may well lose its asymmetry.

A much clearer case for optical instability was obtained when attempts were made to prepare the corresponding active halides of phenylbiphenyl-α-naphthylcarbinol. They were invariably unsuccessful.

It therefore seems probable that only under special conditions can triaryl substituted groups of the above type maintain even momentarily an asymmetric configuration, and whenever a replacement takes place in such a manner as to involve the intermediate formation of a true carbonium ion racemized products will inevitably result. We would explain this optical instability as being due to the inability of the positive ion to maintain its covalent linkages non-planar with the central carbon atom. When the group X is removed from the central carbon atom in these types of compounds, and takes its pair of electrons with it, the remaining valence electrons and their attached groups are in such an energy state that they readily pass through the plane of the carbon atom, and an optically inactive product is produced.

The Spatial Configuration of the Valences in Free Radicals.—The third possible state in which a group containing a tricovalent carbon atom can exist is that of a neutral free radical. Since it was not found possible to prepare optically active triarylmethyl halides, Gomberg's classical method for the preparation of free radicals could not be used in the present study of the optical stability of these tricovalent carbon com-

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(14) Wallis, THIS JOURNAL, **54**, 1695 (1932).

pounds. It was therefore necessary to carry out experiments along somewhat different lines. Schlenk and Herzenstein[15] have reported that triphenylmethyl in some of its reactions behaves like a metallic element. For instance, it undergoes an equilibrium reaction with phenyldibiphenylchloromethane to form triphenylchloromethane and phenyldibiphenylmethyl. It seemed, therefore, that similar reactions could be carried out on *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid. This was found to be the case. Triphenylchloromethane in dry ether was allowed to react with mercury in the presence of *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid. The triphenylmethyl so formed was found to react slowly with the thioglycolic acid derivative. The progress of the reaction could be followed by observing a gradual change of color from yellow to reddish-brown. When this reaction was carried out in a specially constructed polarimeter tube, a gradual decrease of rotation to zero was observed. On admitting air to the apparatus peroxides were formed and precipitated out. These were tested in the polarimeter and found to be inactive. The filtrate was also inactive. Although the reaction did not go to completion, nevertheless optical inactivity resulted. This is undoubtedly due to the fact that the phenylbiphenyl-α-naphthylmethyl formed is unable to maintain its original configuration and therefore racemizes. When this radical returns again to the quadricovalent state as it would do in an equilibrium reaction, the corresponding thioglycolic acid derivative would consist of both *d*- and *l*-forms in equal amounts. Racemization in solution therefore becomes complete. If, as some investigators believe, such free radicals in solution consist of an equilibrium mixture of the benzenoid and quinonoid forms the presence of the latter form would be enough to account for the loss in optical activity in the above experiment. In order to preclude any possibility of tautomerism involving quinonoid forms, experiments were next conducted with aliphatic compounds. Here quinonoidation is obviously impossible.

The Kolbe reaction for the synthesis of hydrocarbons by the electrolysis of the alkali metal salts of fatty acids may be explained by assuming the momentary existence of free radicals. Petersen[16] has shown that when *dl*-methylethylacetic acid is electrolyzed in the form of an aqueous solution of its potassium salt, one of the products of the reaction is a hydrocarbon, 3,4-dimethylhexane. Accordingly Petersen's work was repeated with *l*- and *d*-methylethylacetic acid. In each case the hydrocarbon obtained was optically inactive.

In the Wurtz reaction also the intermediate formation of free radicals has been postulated. Therefore this synthesis was carried out with optically active halides of the type R_1R_2CHX and the hydrocarbon products examined for optical activity. In this case any loss of rotatory power can

(15) Schlenk and Herzenstein, *Ann.*, **394**, 199 (1912).

(16) J. Petersen, *Z. Elektrochem.*, **12**, 141 (1906).

only be due to optical instability of the intermediate free radicals, for Just[17] has shown that the reaction of metallic sodium on optically active halides of the type $R_1R_2CHCH_2X$, in which the halogen is separated from the asymmetric carbon by a CH_2 group, leads to the formation of an optically active 1,1,4,4-tetrasubstituted butane of the same sign of rotation as the original alkyl halide.

The asymmetric molecules chosen for these experiments were *l*- and *d*-α-bromobibenzyl, $C_6H_5CHBrCH_2C_6H_5$, and *d*-2-bromobutane, $C_2H_5CHBrCH_3$. In every case the corresponding hydrocarbon, 1,2,3,4-tetraphenylbutane, or 3,4-dimethylhexane, was found to be inactive. The reactions were carried out in ether solution, at 35 and 20°, respectively, and the products subsequently treated under conditions which ordinarily do not cause racemization; yet optical activity invariably resulted.[18]

From these experiments we may infer that free radicals in general, whether they be of the classical triphenylmethyl type, or of the aliphatic or mixed aliphatic–aromatic type, even though they exist but momentarily, cannot maintain the asymmetric configuration of the corresponding quadricovalent compounds from which they are derived. Furthermore, the experiments with aliphatic radicals show conclusively that at least in these compounds the loss of optical activity cannot be explained on the basis of a tautomeric change to a quinonoid form. It must be concluded that either the three substituents and the central carbon atom become coplanar, or, if a non-planar configuration is maintained, an oscillation of the groups around the central carbon atom takes place and their relative positions in space continuously change.

Experimental Part

Preparation of Methylethylphenylmethylthioglycolic Acid.—This compound was prepared in poor yields by the action of thioglycolic acid on methylethylphenylchloromethane, which was synthesized according to the method of Klages.[19] The chloride obtained from 50 g. of methylethylphenylcarbinol was treated with 35 g. of thioglycolic acid in 50 cc. of toluene, and the solution was refluxed until no more hydrogen chloride was evolved. On cooling the solution colorless crystals precipitated out. Recrystallization of this material from hot water gave a product which melted at 137–138°; yield, 11.8 g. Attempts were made to resolve this acid by means of its brucine and strychnine salts. These were unsuccessful.

Anal. Carius method (I) and Messinger method (II). Calcd. for $C_{12}H_{16}O_2S$: S, 14.29. Found: (I) S, 14.17; (II) S, 14.13.

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[17] Just, *Ann.*, 220, 155 (1883).

[18] The Grignard reaction could also be studied from this point of view, inasmuch as intermediate free radical formation may be postulated when metallic magnesium reacts with an alkyl halide. A survey of the literature, however, showed that Pickard and Kenyon [*J. Chem. Soc.*, 99, 65 (1911)] in attempting to prepare 2-methylbutanol in *d*- and *l*-forms studied the reaction of formaldehyde on the Grignard compound produced by the action of magnesium on *l*-2-iodobutane. No difficulty was encountered in preparing the 2-methylbutanol, but all attempts to prepare it in an optically active condition by this method failed. Although their purpose in investigating such a reaction was different from the one discussed above, yet the results obtained are of interest in this connection.

[19] Klages, *Ber.*, 35, 3507 (1902).

Preparation of 12-Phenyl-12-β-benzoxanthenethioglycolic Acid.—β-Benzoxanthone was prepared by the method of Ullmann.[20] This ketone was caused to react with phenylmagnesium bromide according to Gomberg and Schoepfle.[6] Five times the theoretical amount of phenylmagnesium bromide was used. The mixture was refluxed on the water-bath, with continued stirring, for at least six hours.

12-Phenyl-12-chloro-β-benzoxanthene hydrochloride was prepared from the xanthenol (m. p. 170–171°) according to the directions of Gomberg and Schoepfle.[6] The yields were practically quantitative.

12-Phenyl-12-β-benzoxanthenethioglycolic acid was prepared by refluxing the chloride–hydrochloride in benzene solution with the theoretical quantity of pure thioglycolic acid. After one hour's heating no more hydrogen chloride was evolved. The solution was decolorized with charcoal and the filtrate set aside to cool; colorless crystals, m. p. 187–188°, were obtained; yield, 86%, based on the amount of carbinol taken.

Anal. Carius method. Calcd. for $C_{25}H_{18}O_3S$: S, 8.04. Found: S, 7.99, 8.16. *Mol. wt.*, cryoscopic method in benzene. Calcd.: 398. Found: 402.

Resolution of 12-Phenyl-12-β-benzoxanthenethioglycolic Acid.—Thirty-five and one-half grams of this acid was resolved by fractional crystallization of its brucine salt from acetone. Ten crystallizations gave 6.2 g. of pure material with a constant rotation in acetone $[\alpha]^{20}_D$ −38.2°.

This salt was well pulverized and suspended in 150 cc. of ether in a separatory funnel; 5 cc. of 6 *N* sulfuric acid diluted to 100 cc. was then added, and the whole shaken vigorously until no more solid was visible. The ether layer was separated and *immediately* washed with water until the washings were free from sulfate. This solution was dried with anhydrous sodium sulfate, and the ether evaporated under reduced pressure; 2.3 g. of fine colorless crystals was obtained, m. p. 183–184°; $[\alpha]^{20}_D$ − 48.5° in acetone (*c*, 0.9892 g./100 cc.).

From the mother liquors of the first and second crystallizations was obtained a sample of brucine salt which was treated as described above, except that the ether was allowed to evaporate spontaneously at room temperature. When half of the ether had evaporated, the white crystals which had precipitated were filtered off and found to be optically inactive.[21] The residue obtained by evaporating the remaining ether from the solution was found to give a product which melted at 179°, $[\alpha]^{20}_D$ +28.9° in acetone (*c*, 0.8316 g./100 cc.).

Racemization Experiments on *l*-12-Phenyl-12-β-benzoxanthenethioglycolic Acid.—This acid was found to racemize slowly on standing in acetone solution at 20°. In U. S. P. acetone a sample of the acid was found to lose half of its optical activity in two days; in acetone which had been specially purified the specific rotation fell to half its original value in about five and one-half days.

Long standing in the solid state also causes gradual racemization. One sample of the material decreased in specific rotation from −42.3 to −36.9° in two months, and to −13.9° after fourteen months. This change in rotation was accompanied by a development of a slight orange coloration. Racemization was more rapid when the acid was exposed to light. Heating was found to racemize the acid rather rapidly. When an acetone solution of the compound was refluxed for fifteen minutes the specific rotation decreased from −42.3 to −36.8°. Complete racemization was produced when a sample of the material, dissolved in benzene, was boiled for two hours. This acid is also very sensitive to mineral acids. In one experiment 0.2510 g. was dissolved in 25 cc. of acetone and tested in the polarimeter. Two drops of 6 *N* hydrochloric acid were

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(20) Ullmann, *Ber.*, **38**, 2116 (1905).

(21) A portion of the racemic form of the acid precipitates out, being less soluble in ether than the optically active modification.

then added to this solution, and its rotation determined at several intervals of time. In six hours optical activity had vanished.

The Action of Sodium on *dl*-12-Phenyl-12-β-benzoxanthenethioglycolic Acid in Liquid Ammonia.—The apparatus used, with some simplifications, was that described by Wooster;[22] 1.23 g. of the *dl*-acid was suspended in about 50 cc. of liquid ammonia in a tube immersed in a bath of the same liquid contained in an unsilvered Dewar flask. A current of ammonia gas was continuously circulated through the mixture to ensure thorough stirring and to displace all air from the reaction vessel; 0.25 g. of sodium in the form of small pellets was added from a side-tube. The blue color which at first developed quickly changed to a deep orange-brown. When no more unreacted acid could be seen in the bottom of the tube, 1.25 g. of dry ammonium bromide was added in small portions through another side-tube. A vigorous reaction ensued which resulted in the decolorization of the solution and the formation of a copious white precipitate. The reaction tube was then removed from the cooling bath and the liquid ammonia allowed to evaporate. The residue was taken up in water and washed until the washings were free from halogen and sodium salts. The amorphous white product was dried in air at room temperature. Tests for sulfur were negative. Crystallization of this material, 12-phenyl-β-benzoxanthene, from petroleum ether (60–75°) gave small colorless needles which melted at 153°. Recrystallization from the same solvent failed to raise the melting point.[23]

Anal. Micro method. Calcd. for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.63, 89.42; H, 5.25, 5.73. *Mol. wt.* Calcd.: 308. Found: 300.

Essentially the same method was employed with the *l*-acid as that just described. The reaction was repeated many times, and in every case but one the dry sulfur-free product was found to be optically active in the common organic solvents. In the exceptional case (VII) the solution, after the reaction with sodium, was allowed to stand for a much longer time before the ammonium bromide was added. This indicates that the ion racemizes rather easily. A summary of the results of the various experiments is given.

Run	Acid taken, g.	$[\alpha]^{20}_D$ of sample of acid used	Product taken, g.	$[\alpha]^{20}_D$ of product, 2-dm. tube 25 cc. soln.	$[\alpha]^{20}_D$ product	Solvent
I	2.0	−36.9	0.6015	−0.11	− 2.3	Benzene
II	1.0	−36.9	.1337	− .05	− 4.7	Benzene
III	1.25	−38.2	.2036	− .06	− 3.7	C_2H_5OH
IV	1.25	−38.2	.2032	− .05	− 3.1	C_2H_5OH
V	1.25	−38.2	.2388	− .08	− 4.2	C_2H_5OH
VI	1.23	−48.5	.1812	− .17	−11.7	Acetone
VII	4.0	−41.6	1.6922	.00	0.0	Benzene

Preparation of the sulfur-free levorotatory trisubstituted methane in a crystalline form was not accomplished. All attempts to crystallize the material gave only an amorphous substance. Experiments showed that this compound was easily racemized. Heating of the material in organic solvents produced either a completely inactive material, or one of lower rotation. Samples of the amorphous active compound after it had been made inactive by the above treatment were found to crystallize as before described. The crystals melted at 153°, and were identical with the product obtained from the *dl*-thioglycolic acid derivative.

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[22] Wooster, THIS JOURNAL, 51, 1859 (1929).

[23] Kauffmann and Egner [*Ber.*, 46, 3785 (1913)] claim to have prepared this compound by heating 3-hydroxy-β-naphthyldiphenylcarbinol. Their compound melted at 171° and gave a greenish-yellow color with concentrated sulfuric acid, while the compound prepared by us gives the characteristic deep orange coloration observed when all compounds containing the 12-phenyl-β-benzoxanthenyl radical are treated with this reagent. Although their analytical data check with the requirements of the formula, the method of synthesis would indicate that their compound is a derivative of fluorene and not of xanthene.

Preparation of 12-Phenyl-β-Benzoxanthenyl Ethyl Ether.—One gram of the *l*-acid was dissolved in 90 cc. of absolute alcohol, and to the solution was added 1.2 g. of silver nitrate dissolved in 100 cc. of absolute alcohol. A momentary orange coloration was observed. The light yellow precipitate of silver thioglycolate which formed was filtered off, and the alcoholic filtrate allowed to drip into a liter of distilled water. A white curdy precipitate was immediately produced. This was filtered, washed free of silver ion, and dried in the air; yield of dry sulfur-free product, 0.7212 g. or 88%. This amount of material dissolved in 25 cc. of absolute ether gave no appreciable rotation in a 2-dm. tube. Recrystallization from petroleum ether gave colorless crystals which melted at 118°. This experiment was repeated several times under different conditions but the same inactive product was obtained. Crystallization from an aqueous acetone solution gave crystals which melted at the same temperature as those from petroleum ether.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.18; H, 5.72. Found: C, 84.80; H, 6.02. *Mol. wt.* Carlsohn method. Calcd.: 352. Found: 351.

The corresponding methyl ether was also prepared using a methanol solution; colorless needles (acetone) were obtained which melted at 148°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.21; H, 5.33. Found: C, 85.38; H, 5.64.

Preparation of 12-Phenyl-12-β-benzoxanthenol from the Corresponding Thioglycolic Acid Derivative.—This compound was prepared from the *dl*-acid by a method similar to that above described for the preparation of the ethyl ether, except that acetone and water were used as solvents; yield of crude product, 88%. Crystallization from a mixture of benzene and petroleum ether gave colorless crystals which melted at 170–171°; m. p. by Gomberg and Schoepfle,[6] 171°.

In an entirely similar manner the *l*-acid was converted into the xanthenol. An inactive product was obtained; 0.5706 g. of this compound dissolved in 25 cc. of ether gave no rotation in a 2-dm. tube. Crystallization gave a material which melted at 170–171°.

Preparation of *d*- and *l*-Phenylbiphenyl-α-naphthylcarbinol.—One gram of *d*-phenylbiphenyl-α-naphthylmethylthioglycolic acid[5a] was dissolved in 100 cc. of acetone, and to the solution was added 50 cc. of water. This solution was treated with 1.0 g. of silver nitrate dissolved in 50 cc. of water; yield of product, 0.859 g. Crystallization from aqueous acetone gave colorless crystals which melted at 161–162°, and showed $[\alpha]^{20}_{6563}$ $-3.3°$; $[\alpha]^{20}_{5893}$ $-5.4°$; $[\alpha]^{20}_{5463}$ $-7.6°$ (0.1152 g. of substance in 25 cc. of carbon tetrachloride solution, 2-dm. tube; rotation -0.03, -0.05, $-0.07°$, respectively).

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.13; H, 5.70. Found: C, 90.0; H, 5.9.

In an entirely similar manner 1.0 g. of the *l*-acid was converted into the corresponding carbinol. The product so obtained melted at 160° and showed $[\alpha]^{20}_{5463}$ $+7.2°$ (0.1912 g. in 25 cc. of carbon tetrachloride solution, 2-dm. tube, rotated $+0.11°$).

Preparation of *d*- and *l*-Phenylbiphenyl-α-naphthylmethyl Ethyl Ether.—One gram of the *d*-acid was dissolved in 50 cc. of absolute alcohol (distilled over calcium) and treated with a solution of 1.0 g. of silver nitrate dissolved in 100 cc. of the same solvent. The solutions were mixed slowly and the product worked up as before described. Crystallization from aqueous alcohol gave a compound which melted at 125–126°, and showed $[\alpha]^{20}_{D}$ $+21.7°$ (0.1495 g. of substance in 25 cc. of ether solution, 2-dm. tube, rotated $+0.26°$).

These experiments were repeated on the *l*-acid. A crystalline product was obtained which melted at 125.5–126°, and showed $[\alpha]^{20}_{6563}$ $-17.4°$; $[\alpha]^{20}_{5893}$ $-22.7°$; $[\alpha]^{20}_{5463}$

−27.0; $[\alpha]^{20}_{4863}$ −34.0° (0.1435 g. in 25 cc. of dry ether solution in a 2-dm. tube, rotated −0.20, −0.26, −0.31, −0.39°, respectively).

Anal. Micro method. Calcd. for $C_{31}H_{26}O$: C, 89.85; H, 6.28. Found: C, 89.79, 89.78; H, 6.19, 6.23.

Action of Bromine on *l*- and *d*-Phenylbiphenyl-α-naphthylmethylthioglycolic Acid.—Two grams of the *l*-acid was dissolved in 50 cc. of dry ether and cooled in a bath of solid carbon dioxide and ether. To this solution was added slowly 100 cc. of dry ether containing an equivalent amount of free bromine. A white crystalline precipitate formed almost immediately. A portion of this dried product, dissolved in benzene, showed no rotation; m. p. of crystallized material (benzene) 191°, with decomposition.

Experiments carried out on the *d*-acid gave the same results.

Anal. Carius method. Calcd. for $C_{29}H_{21}Br$: Br, 17.6. Found: Br, 17.8.

Action of Thionyl Chloride on *d*-and *l*-Phenylbiphenyl-α-naphthylcarbinols and their Ethyl Ethers.—One gram of the *d*-carbinol was dissolved in benzene, and to the solution was added the calculated amount of thionyl chloride. To the mixture was added a small amount of petroleum ether (30–60°) and the solution allowed to stand for twelve hours at −6°. Beautifully formed crystals of the chloride, m. p. 194–195°, precipitated out; m. p. (Schlenk)[24] 194.5°. A saturated benzene solution showed no appreciable rotation. Experiments on the *l*-carbinol and the *d*- and *l*-ethyl ethers gave similar results.

Action of Triphenylmethyl on *l*-Phenylbiphenyl-α-naphthylmethylthioglycolic Acid in the Presence of Mercury.—One gram of triphenylchloromethane was dissolved in specially pure dry ether, and to the solution was added 1.0 g. of the *l*-acid, and the total solution made up to 25 cc. It showed a rotation at 20° in a 2-dm. tube with the 6563 line of −0.98°. This solution was placed in a specially constructed apparatus and shaken with mercury in the absence of oxygen for twenty-four hours. The solution was then allowed to stand in contact with mercury for fourteen days in the dark. After this time had elapsed the rotatory power of the solution was again determined in a specially constructed 2-dm. polarimeter tube. Other readings were taken from time to time: fourteen days −0.59°; nineteen days −0.39°; twenty-three days −0.19°; 27 days −0.02°. During this time the color of the solution changed from yellow to reddish-brown. The solution was removed and allowed to come into contact with air. The brown color quickly disappeared, and the solution became nearly colorless. The precipitated peroxides were filtered and found to be optically inactive. The filtrate also showed no appreciable rotation.

Electrolysis of *l*- and *d*-Methylethylacetic Acid.—Fifty grams of the *l*-acid, previously resolved by the method of Schütz and Marckwald[25] (rotation without solvent at 20°, D line, 2-dm. tube, −12.25°) was converted into its potassium salt and electrolyzed according to the method used by Petersen[16] for the *dl*-acid. After thirty-one hours seven grams of a yellow oily product was obtained. This oil after treatment and purification according to Petersen's method gave a hydrocarbon which was found to be inactive. The experiment was repeated with the *d*-acid. Similar results were obtained. The boiling point of the hydrocarbon produced was 110–116°. The b. p. of 3,4-dimethylhexane recorded in the literature is 116° (Norris and Green).

Preparation of 1,2,3,4-Tetraphenylbutane.—Phenylbenzylcarbinol was resolved into its pure dextro and mixed levo modifications by the method of Gerard and Kenyon;[26] 4 g. of the dextro compound (m. p. 67°, $[\alpha]^{22}_{D}$ +52.0 in alcohol, *c* 1.780 g. per 100 cc.), was dissolved in 50 cc. of benzene. The solution was cooled to 0° and saturated with

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(24) Schlenk, *Ann.*, 394, 196 (1912).

(25) Schütz and Marckwald, *Ber.*, 29, 52 (1896).

(26) Gerard and Kenyon, *J. Chem. Soc.*, 2564 (1928).

pure hydrogen bromide gas. Purification of the product by the usual methods gave a levorotatory bromide which was a viscous yellow oil. This was not distilled because of possible decomposition; d_{21}^{21} 1.316; $[\alpha]_D^{22}$ −27.1° in absolute alcohol (c 1.642 g. per 100 cc.). In a similar manner a *dl*- and a mixed dextrorotatory α-bromobibenzyl were prepared. The mixed *d*-compound showed a rotation at 22° of +2.69° in a 0.5-dm. tube without solvent, D line.

Anal. *l*-Bromide, Parr Bomb and Volhard Titration. Calcd. for $C_{14}H_{13}Br$: Br. 30.62. Found: Br, 29.41.[27]

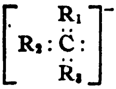
4.0 g. of *l*-α-bromobibenzyl was dissolved in absolute ether, and to the solution was added 3 g. of sodium in the form of small shot. The mixture was refluxed on the water-bath until the ether solution gave no test for bromine. This required about eight hours. The ether was then filtered off, and the residue treated with alcohol, diluted with water, and extracted with ether. The combined ether solutions were dried with calcium chloride and concentrated to 20 cc. Colorless bromine-free crystals precipitated out; 0.1586 g. of this material in 25 cc. of acetone solution gave no rotation in a 2-dm. tube. Recrystallization of the compound from alcohol gave needles which melted sharply at 178°.

The experiment was repeated with the mixed *d*-α-bromobibenzyl. Similar results were obtained. The crystalline material melted at 178° and was inactive. The *dl*-bromide also gave a product which melted at 178°.[28]

Anal. Calcd. for $C_{28}H_{26}$: C, 92.76; H, 7.24. Found: C, 92.59; H, 7.37. *Mol. wt.* (I) Rast Method, (II) Carlsohn Method. Calcd.: 362. Found: (I) 373, (II) 342.

Preparation of 3,4-Dimethylhexane by the Wurtz Reaction.—*d*-2-Bromobutane was prepared from an incompletely resolved *l*-*sec*-butyl alcohol according to the directions of Levene and Marker.[29] It had a specific rotation $[\alpha]_D^{22}$ +10.70° without solvent. Levene and Marker reported $[\alpha]_D^{25}$ +10.81° for the bromide; 8 g. of this material was dissolved in dry ether and treated at room temperature with metallic sodium according to the method of Norris and Green.[30] After the reaction was complete, the bromine-free ether solution was tested in the polarimeter. It gave no rotation. By fractionation a hydrocarbon was obtained which boiled at 115–117°. Examination of this material in the polarimeter showed that it was completely inactive; b. p. (Norris and Green) 116°.

Summary

12-Phenyl-12-β-benzoxanthenethioglycolic acid (IV) has been synthesized and resolved into pure *levo* and mixed *dextro* modifications. The *levo* form has a specific rotation $[\alpha]_D^{20}$ −48.5°. Evidence is submitted which shows that a carbanion of the type  $\left[\begin{array}{c} R_1 \\ R_2:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}: \\ R_3 \end{array}\right]^-$ is spatially sufficiently stable to maintain an asymmetric configuration. The three substituents and the central carbon atom, therefore, cannot lie in the same plane.

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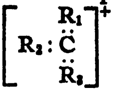
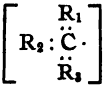
[27] The low value for the bromine in this analysis is undoubtedly due to the presence of small amounts of unchanged carbinol or traces of benzene, since the product was not purified by distillation.

[28] Fromm and Achert [*Ber.*, **36**, 539 (1903)] have prepared a compound, m. p. 255°, by heating benzyl sulfide. To this compound was assigned the structure of 1,2,3,4-tetraphenylbutane. R. Bacon [*Philip. J. Sci.*, **4A**, 166 (1909)] prepared the same compound by heating benzyl chloride with potassium oxalate in a sealed tube. Both these syntheses, however, leave much doubt as to the actual structure of the compound these investigators prepared.

[29] Levene and Marker, *J. Biol. Chem.*, **91**, 405 (1931).

[30] Norris and Green, *Am. Chem. J.*, **26**, 313 (1901). These investigators used the *dl*-bromide.

The stability of the spatial arrangement of the groups in tricovalent carbonium ions,  $\left[R_2:\overset{R_1}{\underset{R_3}{\underset{\cdot\cdot}{\ddot{C}}}}\right]^+$ has been studied, and evidence has been submitted which indicates that in the absence of a special mechanism which leads to Walden inversion such configurations are optically unstable.

The optical instability of free radicals  $\left[R_2:\overset{R_1}{\underset{R_3}{\underset{\cdot\cdot}{\ddot{C}}}}\cdot\right]$ has been demonstrated: by the loss of optical activity when *l*-phenylbiphenyl-α-naphthylmethylthioglycolic acid was allowed to react with triphenylmethyl; by the production of an inactive hydrocarbon in the electrolysis of *l*- and *d*-potassium methylethylacetate; and by the production of an inactive hydrocarbon by the action of metallic sodium on *d*- and *l*-α-bromobibenzyl and *d*-2-bromobutane.

A discussion of these results is given in the light of certain theories which have been proposed for the constitution of these tricovalent compounds.

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE LABORATORIES OF THE UNIVERSITY OF BUFFALO]

Radical Interchange on the Part of Certain Alkyl Orthoformates[1]

BY HOWARD W. POST AND EDWIN R. ERICKSON

Early work on aliphatic ortho esters, while outlining their preparation and properties, has mentioned as well their instability. Triethyl orthoformate for example is not as stable as are the orthoformates of the higher aliphatic alcohols, but no further suggestions have been advanced on this point to date. Compounds of this type have been prepared from the corresponding alcoholate[2] and from the alcohol and hydrogen cyanide.[3]

It was our original purpose to test the relative reactivity of some alcoholates of simple aliphatic alcohols by mixing one mole of chloroform with three moles each of two different alcoholates and determining the identities of the products but the problem soon resolved itself into a study of the reaction

$$HC(OR)_3 + HC(OR')_3 \rightleftharpoons HC(OR)_2OR' + HC(OR')_2OR \qquad (1)$$

The Reaction of Chloroform with Alcoholate Mixtures.—One equivalent of chloroform was added to a mixture of 1.5 equivalents each of two aliphatic alcoholates, the system being stirred gently. These proportions gave better yields than 1:3:3. The results are summarized below.

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(1) Presented at the Spring Meeting, American Chemical Society, March, 1933, at Washington, D. C.

(2) Deutsch, *Ber.*, **12**, 117 (1897); Claisen, *ibid.*, **31**, 1010 (1898); Sah and Ma, THIS JOURNAL, **54**, 2964 (1932); "Organic Syntheses," Vol. V, 1925, p. 55.

(3) Pinner, *Ber.*, **16**, 356 and 1643 (1883).

TABLE I

$CHCl_3 + RONa + R'ONa$

	R	R'	$HC(OR)_3$, %	$HC(OR)_2OR'$, %	$HC(OR')_2OR$, %	$HC(OR')_3$, %	Total yield, %
1	C_3H_7-	C_4H_9-	27.4	26.0[a]	31.6[a]	15.0	55.0
2	C_3H_7-	*i*-C_5H_{11}-	28.0	29.8	32.3	9.9	41.0
3	C_3H_7-	C_5H_{11}-	23.9	32.3[a]	30.9[a]	12.9	50.2
4	C_2H_5-	C_4H_9-	12.6	42.1[a]	35.9[a]	9.4	42.1
5	C_2H_5-	C_3H_7-	2.7	41.9	39.5	16.1	34.0

[a] Identified by boiling point only.

It will be noted that in any reaction such as indicated in Equation 1 using the alcoholates specified in Table I there is a strong tendency for the mixed esters to form at the expense of those whose alkyl radicals are all alike.

The physical constants of these simple and mixed orthoformates may be found in the literature[2] and for purposes of identification we confined ourselves to determinations of boiling points, refractive indices and densities. It was found necessary to determine refractive index and density immediately after distillation to obtain consistent results.

TABLE II

PHYSICAL DATA

Ester	B. p., °C.	n_D^{20}	d_4^{21}	Mol. wt. Calcd.	Mol. wt. Found
$HC(OC_2H_5)_3$	145 (747 mm.) 60 (30 mm.)	1.3915	0.8964	148.13	148.6
$HC(OC_2H_5)_2OC_3H_7$	165 (747 mm.) 81 (30 mm.)	1.3989	.8813	162.1	160.6
$HC(OC_2H_5)_2SC_2H_5$	76–80 (17 mm.)	1.4397	.9451 (20°/4°)	164.2	165.7
$HC(OC_3H_7)_3$	190–191 (745 mm.) 93 (30 mm.)	1.408	.879	190.2	189.9
$HC(OC_3H_7)_2OC_2H_5$	184 (745 mm.) 93 (30 mm.)	1.4031	.8973 (22°/4°)	176.2	175.5
$HC(OC_3H_7)_2OC_5H_{11}$-*i*	124–130 (24 mm.)	1.415	.8647	218.2	216.0
$HC(OC_5H_{11}$-*i*$)_3$	166 (25 mm.)	1.4242	.858	274.3	272.2
$HC(OC_5H_{11}$-*i*$)_2OC_3H_7$	140–147 (30 mm.)	1.4194	.8626	246.2	244.4

Using the formula $N = M(n^2 - 1)/d(n^2 + 2)$.

After standing for thirty days samples of mixed esters when distilled gave fractions which identified by boiling points, refractive indices and densities represented all four possibilities—$HC(OR)_3$, $HC(OR)_2OR'$, $HC(OR')_2OR$ and $HC(OR')_3$. This reaction took place in the case of every mixed ester prepared during the course of this work.

A mixture of pure $HC(OC_3H_7)_3$ and pure $HC(OC_5H_{11}$-*i*$)_3$ in equimolar amounts was set aside to stand for one month at room temperature. At the end of that time fractional distillation at low pressures showed that an interchange of radicals had taken place but that the two middle fractions were not present in as large amount as the first and fourth

$$HC(OC_3H_7)_3 + HC(OC_5H_{11}\text{-}i)_3 \rightleftharpoons HC(OC_3H_7)_2OC_5H_{11}\text{-}i + HC(OC_5H_{11}\text{-}i)_2OC_3H_7 \quad (2)$$

Diethyl propyl orthoformate reacted in the presence of phosphorus pentoxide to give all four possible orthoformates. It may seem at first that the interaction of two molecules of this ester under these conditions may have been catalyzed by hydrogen ion, but this can hardly be so because the pure orthoformates containing like alkyl groups did not hydrolyze when similarly treated. With only a small amount of water present, hydrolysis does take place, however.

Propyl orthoformate reacted with absolute ethyl alcohol to give four possibilities as well as the two alcohols

$$HC(OC_3H_7)_3 + C_2H_5OH \rightleftharpoons C_3H_7OH + HC(OC_3H_7)_2OC_2H_5, \text{ etc.} \quad (3)$$

Yields were: $HC(OC_2H_5)_3$ 2.1%, $HC(OC_2H_5)_2OC_3H_7$ 42.0%, $HC(OC_3H_7)_2$-OC_2H_5 40.0% and $HC(OC_3H_7)_3$ 15.9%. Of course it is probable here that as soon as more than one orthoformate appears it may react with some other orthoformate as well as with one of the alcohols.

Ethyl mercaptan was allowed to stand in contact with triethyl orthoformate in a sealed tube at room temperature for one week. On distillation triethyl orthoformate and monothiotriethyl orthoformate came over. There was a higher boiling fraction but we were not able to isolate anything therefrom

$$HC(OC_2H_5)_3 + C_2H_5SH \rightleftharpoons C_2H_5OH + HC(OC_2H_5)_2SC_2H_5 \quad (4)$$

Experimental Part

Preparation of the Mixed Esters.—The alcohols were purchased from the Eastman Kodak Co. and then dehydrated. To prepare the alcoholates 3 equivalents of clean sodium was dissolved in an excess of the desired alcohol, and the two solutions of alcoholates were mixed. To this system a solution of chloroform in a little mixed alcohols was added dropwise with gentle stirring. All outlets of the system were closed with calcium chloride tubes. Care must be taken lest the temperature rise too high. The reaction was completed in about an hour and a half but it was found that the yield could be increased by allowing the mixture to stand several hours longer. Half a gram of hydroquinone acts as an inhibitor of oxidation here.

Sodium chloride was removed by suction, excess alcohols distilled at atmospheric pressure and the mixture of products fractionated at reduced pressures, generally 30 mm. Refractionations gave pure products.

Reactions of Esters.—The reactions of the mixed esters were brought about simply by allowing them to stand as already described.

Molecular refractions were calculated from the values for the various atoms found in the current literature.[4]

Discussion

We have shown that an equilibrium is immediately set up when two different orthoformates are mixed at room temperatures. This equilibrium reaction consists of the interconversion of the four esters $HC(OR)_3$, HC-

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(4) Landolt and Börnstein, "Physikalisch-chemische Tabellen," Vol. II, p. 985 (5th ed.).

$(OR')_2OR$, $HC(OR)_2OR'$ and $HC(OR')_3$. Only a small amount of the two mixed esters is obtained when propyl orthoformate and isoamyl orthoformate are mixed, as compared with a larger amount of the two mixed compounds using esters of lower molecular weights. This may be explained by assuming that reaction is preceded by decomposition into fragments, this decomposition being known to be less rapid in the case of the higher homologs. Similar reactions with alcohols and mercaptans seem to involve transfer of OR rather than R.

Summary

1. At room temperatures the mixed orthoformates thus far investigated isomerize to a mixture of all four possible esters, this reaction taking place almost instantaneously over phosphorus pentoxide.

2. At room temperatures two orthoformates react with interchange of radicals, the yield of products varying, as far as observation has gone, inversely as the radical weights involved.

3. Tripropyl orthoformate reacts with absolute ethyl alcohol, giving a mixture of the four possible orthoformates and two alcohols. Ethyl mercaptan reacts with triethyl orthoformate giving the mono thio compound.

BUFFALO, N. Y.

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[CONTRIBUTION FROM THOMAS AND HOCHWALT LABORATORIES, INC.]

Polymerization of Diolefins with Olefins. II. Function of Pentene-2 in the Polymerization of Isoprene

BY CHAS. ALLEN THOMAS AND WM. H. CARMODY

In the previous paper[1] it was reported that when pure isoprene, in which there was no appreciable amount of olefin present, was placed in contact with anhydrous aluminum chloride, there was no temperature rise or any other obvious chemical reaction, even when a considerable proportion of anhydrous aluminum chloride had been added. It was shown that an olefin, such as pentene-2, added to the isoprene–aluminum chloride mix, started the reaction immediately; and that in polymerizing isoprene and pentene-2 by aluminum chloride, there were two solid polymers formed, one insoluble and the other soluble in hydrocarbon solvents. The amount of the soluble polymer formed is proportional to the pentene-2 present, while the amount of the insoluble polymer varies inversely with the amount of pentene-2 present.

The purer the isoprene, the more inert it is toward aluminum chloride. Very pure isoprene can be obtained by converting it into the tetrabromide and regenerating it with zinc dust according to Whitby and Crozier.[2] Several hours of contact of this pure isoprene with anhydrous aluminum chloride causes the formation of small bubbles which are immediately followed by a spongy polymeric growth. A few days later there are masses of this polymer, insoluble in the water-white isoprene. The majority of the isoprene is slowly converted into this gelatinous mass, analysis of which shows it to be $(C_5H_8)_x$, identical with the insoluble polymer previously described.

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[1] Thomas and Carmody, THIS JOURNAL, 54, 2480 (1932).

Large quantities of dry hydrogen chloride, bubbled through isoprene containing aluminum chloride, cause the reaction to become violent. Fifty cc. of isoprene in 250 cc. of naphtha was stirred rapidly in a cooled vessel while 10 g. of aluminum chloride was added in portions. A slow stream of dry hydrogen chloride gas was led below the surface of the mixture and polymerization was continued for three and one-half hours, after which the polymers were recovered in the manner previously reported. There was obtained 21 g. of soluble polymer and 12.4 g. of insoluble. Hence it can be seen that dry hydrogen chloride gas, beside initiating the polymerization of isoprene, greatly influences the yields of soluble and insoluble polymers.

Isoprene hydrochloride, formed by passing hydrogen chloride into isoprene, reacts with aluminum chloride to form a complex which is soluble in isoprene. This suggested that the soluble polymer is produced in relation to the isoprene hydrochloride present; and when enough is present to dissolve completely the aluminum chloride then only soluble polymer is produced. This point was further substantiated when it was found that only the soluble polymer was formed when isoprene hydrochloride was added to a reaction mixture of isoprene and aluminum chloride.

Other mutual solvents for isoprene and aluminum chloride increase the yield of soluble and decrease the insoluble polymers. When 5 g. of aluminum chloride is dissolved in 45 g. of nitrobenzene and this solution added to isoprene there is obtained soluble polymer only. If a diluent, such as petroleum naphtha, is used with the isoprene, the aluminum chloride is partly thrown out of solution and some insoluble polymer is obtained. Ethyl acetate forms with aluminum chloride, an isoprene soluble complex. By running a series of identical polymerizations with the exception of increasing by small amounts ethyl acetate added to the reaction mixture, it is found that there is an exact relation between yield of soluble polymer and the amount of ethyl acetate added. This relationship is much the same as when pentene-2 is added to isoprene.

It is assumed that the soluble and insoluble polymers differ in molecular weight alone, and it is evident that the more aluminum chloride put into solution, the lower the molecular weight of the polymer obtained. When

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(2) Whitby and Crozier, *Can. J. Research*, 6, 212 (1932)

no mutual solvent for the isoprene and aluminum chloride is employed the polymerization is initiated on the surface of the catalyst. With solid aluminum chloride, the surface comparable to molecular dispersement, is small when referred to the same mass of aluminum chloride in solution as a complex. Thus, with solid aluminum chloride, not many polymer growths are started, and after prolonged contact the polymers have an opportunity to grow to large size and become insoluble. When the catalyst is in solution, giving molecular contact, many polymer growths are started and these are so numerous that with the available isoprene they do not grow to high molecular weight, thus producing the soluble polymer. This theory of short chain formation has independently been advanced by Houtz and Adkins in their work with styrene.[3]

Previous work showed that in the polymerization of isoprene with pentene-2, the more olefin present the lower the molecular weight of the polymers. This suggests that the pentene-2 is not interreacting with the isoprene, but is present in the role of mutual solvent. Even though pentene-2 and aluminum chloride form a complex, it is immaterial to the theory so long as a solution of the catalyst in the isoprene is obtained. If isoprene was treated with pentene–aluminum chloride complex, and never allowed to be in contact with the solid catalyst, then there should be obtained a minimum of insoluble polymers and a maximum of soluble polymers.

One mole of pentene-2 in 400 cc. of naphtha was stirred violently, while 40 g. of anhydrous aluminum chloride was added portionwise during two and one-half hours, at a temperature between 0 and 5°. Agitation was continued for an additional hour, when most of the aluminum chloride had reacted with the pentene-2; 1 mole of pure isoprene was added over a period of two and one-half hours. Much heat was evolved, and additional cooling was necessary to keep the mixture below 30°. The mixture was neutralized and finished in the usual manner. There was obtained 71.2 g. of soluble polymer and only 1.2 g. of the insoluble polymer.

Summary

1. In polymerization of isoprene by solid aluminum chloride, largely insoluble polymer is formed.

2. When the aluminum chloride is put into solution as a complex in the isoprene, largely a soluble polymer is produced.

3. Pentene-2 acts only as a "solubilizer" for the aluminum chloride when polymerized with isoprene, thus producing a low molecular weight or soluble polymer.

4. A theory for the above is suggested.

DAYTON, OHIO

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[3] Houtz and Adkins, THIS JOURNAL, 55, 1609 (1933).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Retropinacolone Rearrangement. I

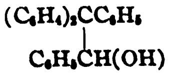
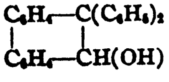
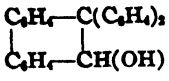
BY W. E. BACHMANN

Delacre[1] found that *as*-tetraphenylethyl alcohol is converted to tetraphenylethylene when it is heated with acetyl chloride at 200° in a sealed tube. We have now undertaken an investigation of the reaction in order to learn whether the reaction is general for the whole class of tetraarylethanols and also to discover if the rearrangement can be employed to determine the relative migration aptitudes of aryl groups.

An attempt was made to rearrange *as*-tetraphenylethyl alcohol by heating it with acetyl chloride at ordinary pressure; under these conditions tetraphenylethyl acetate was formed. We then tried the action of a solution of iodine in acetic acid, which is an excellent rearranging agent for pinacols;[2] it was found that tetraarylethanols are rapidly and completely rearranged when they are heated with iodine and acetic acid at ordinary pressure.

If a mixed tetraarylethanol of the type $R_1R_1R_2CCH(OH)R_2$ is subjected to rearrangement, two courses are open since either R_1 or R_2 can migrate. From the relative amounts of the two ethylenes that are formed it is possible to determine the extent to which each group migrated in the rearrangement. We have prepared and rearranged three tetraarylethanols of this type; namely, 1,2-diphenyl-2-biphenyleneëthanol (IV), 10,10-diphenylphenanthrol-9 (V) and 10-biphenylenephenanthrol-9 (VI). The results of the rearrangements are presented in Table I.

TABLE I

No.	Ethanol	Group migrated	Yield, %	Products
I	$(C_6H_5)_3CCH(OH)C_6H_5$		100	Tetraphenylethylene
II	$(CH_3C_6H_4)_3CCH(OH)C_6H_4CH_3$		100	Tetra-*p*-tolylethylene
III	$(CH_3OC_6H_4)_3CCH(OH)C_6H_4OCH_3$		100	Tetraanisylethylene
IV	 $(C_6H_4)_2CC_6H_5$ $C_6H_5CH(OH)$	Phenyl	0	Diphenylbiphenyleneethylene
		Biphenylene	100	9,10-Diphenylphenanthrene
V	 $C_6H_4—C(C_6H_5)_2$ $C_6H_4—CH(OH)$	Phenyl	100	9,10-Diphenylphenanthrene
		Biphenylene	0	Diphenylbiphenyleneethylene
VI	 $C_6H_4—C(C_6H_4)_2$ $C_6H_4—CH(OH)$		0	Dibiphenyleneëthylene
		Biphenylene	100	9,10-Biphenylenephenanthrene

It is noteworthy that only a single rearrangement product is obtained from the three mixed ethanols. It appears that the formation of the phenanthrene ring is favored, for the same product 9,10-diphenylphen-

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(1) Delacre, *Bull. acad. roy. Belg.*, [3] **20**, 109 (1890).

(2) Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

anthrene is produced from two different ethanols, 1,2-diphenyl-2-biphenylene-ethanol (IV) and 10,10-diphenylphenanthrol-9 (V). Werner and Grob[3] obtained similar products by the interaction of hydrogen iodide and the pinacolones corresponding to the mixed ethanols; they postulated the intermediate formation of the ethanols in the reaction.

In a future communication will be reported the results obtained with a large number of aryl groups.

Experimental

Preparation of Tetraarylethanols.—We prepared the tetraarylethanols by reduction of pinacolones by isopropylmagnesium iodide[4] and bromide. To a solution of the Grignard reagent prepared from 5 cc. of isopropyl iodide in 20 cc. of ether was added 20 cc. of benzene and then 0.02 g. mole of solid pinacolone in portions; the reaction usually took place at once with evolution of gas. After being refluxed, the mixture was hydrolyzed; all of the compounds were obtained as colorless crystals. The essential data are given in Table II.

YIELDS AND PROPERTIES OF TETRAARYLETHANOLS

Abbreviations: alc, alcohol; ac, acetone; bz, benzene; ch, chloroform; h, hot; v, very; s, soluble; sls, slightly soluble; i, insoluble or very slightly soluble

Ethanol	Time, hrs.	Yield, %	Rec. solv.	Cryst. form	M p., °C.	Solubility			Analyses, %	
						alc	ac	ch	Calcd.	Found
1,2,2,2-Tetra-phenyl-	1.0	95	Ch + alc	Plates	150 151					
1,2,2,2-Tetra-*p*-tolyl-[a]	0.5	98	Ac + alc	Heavy needles	161-162	sls	vs		C, 88.7 H, 7.4	88 1 7.6
1,2,2,2-Tetra-anisyl-	1.0	60	Ch + alc	Heavy needles	148-150	sls	vs	s	C, 76.6 H, 6.4	76.0 6.4
1,2-Diphenyl-2-biphenylene	0.2	72	Ac + alc	Cubes	159–160	sls	vs		C, 89.7 H, 5.8	89.7 5.9
10,10-Diphenylphen-anthrol-9	0.8	93	Ch + alc	Prisms	205–206	i		s	C, 89.7 H, 5.8	89 2 6.0
10-Biphenylenephen-anthrol-9	0.2	50	Ac + alc	Clusters needles	177–178	sls	vs (h)		C, 90.2 H, 5 2	90.1 5.3

[a] The ethanol crystallizes from alcohol with solvent of crystallization.

Rearrangement of Tetraarylethanols.—A solution of 1.0 g. of tetraarylethanol and 0.05 g. of iodine in 10 cc. of acetic acid was refluxed for one hour. In several cases a large proportion of the rearrangement product precipitated from the solution after a few minutes; if the mixture bumped badly more solvent was added. The mixture was cooled slightly and treated with 5 cc. of alcohol saturated with sulfur dioxide. On being chilled the solution deposited the rearrangement product in the form of colorless crystals. The yields of the products were quantitative, showing that no side reactions occurred. The properties of the products with the exception of tetra-*p*-tolylethylene agreed with those described in the literature. Our tetra-*p*-tolylethylene crystallized in colorless needles and melted at 142°; Staudinger and Goldstein[5] reported a melting point of 151°.

Anal. Calcd. for $C_{30}H_{28}$: C, 92.8; H, 7.2. Found: C, 93.3; H, 7.5.

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(3) Werner and Grob, *Ber.*, **37**, 2895 (1904).

(4) Gorski, *J. Russ. Phys.-Chem. Soc.*, **45**, 163 (1913).

(5) Staudinger and Goldstein, *Ber.*, **49**, 1925 (1916).

A portion of our tetra-*p*-tolylethylene was reduced to the corresponding ethane by treating a boiling solution of 0.35 g. of the ethylene in 10 cc. of amyl alcohol with 0.5 g. of sodium cut in small pieces. After ten minutes water was added and the product was taken up in benzene; concentration of the solution deposited the *s*-tetra-*p*-tolylethane in colorless prisms; m. p. 278–279°; yield, 95%. The ethane is little soluble in hot alcohol or in cold benzene; it is soluble in hot benzene.

Anal. Calcd. for $C_{30}H_{30}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.8.

s-Tetra-*p*-tolylethane was synthesized by heating a mixture of 1.1 g. of di-*p*-tolylbromomethane and 0.05 g. of magnesium ribbon in 5 cc. of ether and 5 cc. of benzene for twenty hours; yield, 50%; m. p. 278–279°; the product so obtained was identical in all respects with the product produced by reduction of the ethylene.

Tetraphenylethyl Acetate, $(C_6H_5)_2CCH(OCOCH_3)C_6H_5$.—A mixture of 1.0 g. of *as*-tetraphenylethyl alcohol, 10 cc. of acetyl chloride and 5 cc. of benzene was refluxed for ten hours. The product obtained by evaporation of the solvents was recrystallized from a mixture of benzene and alcohol; colorless needles; m. p. 151°; yield, 1.11 g. (99%); Delacre[1] reported a m. p. of 131°. Tetraphenylethyl acetate is little soluble in cold alcohol or acetic acid; it is readily soluble in hot benzene and in hot acetic acid.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.7; H, 6.1. Found: C, 85.7; H, 6.3.

A 0.1-g. portion of tetraphenylethyl acetate was warmed for a few minutes with a mixture of 1 cc. of 40% potassium hydroxide and 2 cc. of alcohol; this treatment hydrolyzed the ester to acetic acid and tetraphenylethyl alcohol; the latter was then cleaved into triphenylmethane[1] and benzaldehyde. When the ester was heated with acetic acid and iodine for a few minutes, rearrangement to tetraphenylethylene took place.

Summary

as-Tetraphenylethyl alcohol is dehydrated and rearranged to tetraphenylethylene when it is heated with a solution of iodine in acetic acid. Five new tetraarylethanols have been synthesized and subjected to the retropinacolone rearrangement.

ANN ARBOR, MICHIGAN

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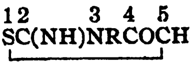
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KANSAS]

The Alkyl Derivatives of the Mono Substituted Thiazolidones. I

BY F. B. DAINS AND FLOYD EBERLY

Some years ago Beckurts and Frerich[1] published a paper on the ethylation of the monoarylthiazolidones which were prepared by the action of potassium thiocyanate upon the chloracet derivatives of various monoarylamines. Several intermediate products were described, but the ones used in their investigation were regarded as 2-imino-3-aryl-4-thiazolidones. The reason given for this structure was that on hydrolysis 3-aryl-2,4-thiazolediones were formed.


$$\overset{1}{S}\overset{2}{C}(NH)\overset{3}{N}R\overset{4}{C}O\overset{5}{C}H_2$$

Wheeler and Johnson[2] have shown in an exhaustive study that this

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(1) Beckurts and Frerich, *Arch. Pharm.*, **253**, 233–65 (1915).

(2) Wheeler and Johnson, *Am. Chem. J.*, **28**, 121–128 (1902).

formula of Beckurts and Frerich represented a labile form which rearranged to the stable 2-arylamino(or imino)-thiazolidone. This on hydrolysis gave both the unsubstituted 2,4-thiazoledione and the 3-aryl diketo product obtained by Beckurts and Frerich. They assumed[3] that the two compounds resulted from the hydrolysis of an intermediate aryl thiohydantoic acid, the ring again closing after the loss of aniline or ammonia.

We have found that a benzal group at 5 stabilized the ring and that on hydrolysis a 5-benzal-2,4-thiazoledione resulted and not a 3-aryl diketo compound which would be necessitated by the formula of Beckurts and Frerich.

These authors by the ethylation of the sodium salts of the thiazolidones obtained mono ethyl derivatives which were assumed to be 2-ethylimino-3-aryl-4-thiazolidones, $\underline{\mathrm{SC(NC_2H_5)NRCOCH_2}}$. Wheeler and Johnson[4] had made the observation that the stable phenylthiazolidone in alkaline solution with benzyl chloride gave 2-phenyl-2-benzylaminothiazolidone, a fact not in harmony with the above assumption. The following experimental work has confirmed the Wheeler–Johnson formula for the stable hydantoins (as 2-aryl derivatives). It has also been shown that alkylation of the monoarylthiazolidones gave two isomers: one the 2-aryl-2-alkyl compound and the other a 2-aryl-3-alkylthiazolidone which corresponded to the Beckurts–Frerich idea but with the aryl and alkyl groups reversed in position.

Experimental

2-*p*-Bromophenylaminothiazolidone.—*p*-Bromoaniline (1 mole) was dissolved in acetone (300 cc.) and pyridine (96 g.) in a flask fitted with an air condenser and cooled in ice water. To this mixture was added slowly chloroacetyl chloride (135 g.) with constant agitation. After standing for an hour, water was added and the ω-chloro-*p*-bromoacetanilide was filtered, washed and dried. Crystallization from alcohol gave a pure product (m. p. 178°).[5] The chloroacetyl compound (135 g.) and potassium thiocyanate (60 g.) were dissolved in alcohol (300 cc.) and refluxed for twenty hours. The yield of crude thiazolidone was nearly the theoretical. From glacial acetic acid, the pale yellow needles melted at 224°.

Anal. Calcd. for $C_9H_7BrN_2OS$: N, 10.35. Found: N, 9.96.

The 5-benzal derivative did not melt at 310° (N, 7.80. Found: N, 7.57). The thiazolidone (m. p. 224°) was soluble in hot 5% sodium hydroxide and on cooling the yellow sodium salt crystallized out.

Ethylation of the Sodium Salt.—The dry salt was dissolved in alcohol with a slight molar excess of ethyl iodide and refluxed for ten hours. After removal of the alcohol and excess of ethyl iodide with steam, the residue was dissolved in ether. The ethereal solution was extracted repeatedly with hydrochloric acid (10%). On neutralizing the acid solution there was obtained 2-ethyl-2-*p*-bromophenylamino-4-thiazolidone; the white needles from ligroin melted at 121°.

Anal. Calcd. for $C_{11}H_{11}BrN_2OS$: N, 9.36. Found: N, 9.42.

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(3) Ref. 2, p. 124.

(4) Ref. 2, p. 146.

(5) Beckurts and Frerich, *Arch. Pharm.*, 241, 212 (1903). The above seems to give better yields than the methods recorded in the literature for the preparation of these chloroacet derivatives.

Proof of Constitution.—The compound (m. p. 121°) was hydrolyzed by boiling with sulfuric acid (50%) for several hours. The mixture was made alkaline with sodium hydroxide and distilled with steam. Ammonia was evolved and an oil, ethyl-*p*-bromoaniline, appeared in the distillate. This oil with phenyl isocyanate gave α-ethyl-α-*p*-bromophenyl-β-phenyl urea; the rhombic crystals from alcohol melted at 108°.

Anal. Calcd. for $C_{15}H_{15}BrN_2O$: N, 8.77. Found: N, 8.62.

For comparison ethyl-*p*-bromophenylamine was made by the action of diethyl sulfate on powdered *p*-bromoaniline at 50°. The fraction of b. p. 146–152° (25 mm.) gave with phenyl isocyanate the same urea (m. p. 108°). Also the same benzoyl-*p*-bromoanilide, m. p. 88°, was obtained from both amines.

Anal. Calcd. for $C_{15}H_{14}BrNO$: N, 4.60. Found: N, 4.66.

***p*-Bromophenyl Ethyl Cyanamide, $BrC_6H_4N(CN)C_2H_5$.**—The residue in the steam distillation flask contained a small amount of the above compound; colorless plates from alcohol which melted at 78°.

Anal. Calcd. for $C_9H_9BrN_2$: N, 12.44. Found: N, 12.42.

It was identical with a synthetic preparation made from ethyl-*p*-bromophenylamine, bromine and potassium cyanide. This cyanamide was also obtained easily by the action of sodium hydroxide (20%) upon the ethyl thiazolidone.

The ethyl thiazolidone (m. p. 121°) condensed with benzaldehyde in hot alcohol solution using piperidine or a few drops of sodium hydroxide and gave a 5-benzal derivative (m. p. 225°).

Anal. Calcd. for $C_{18}H_{15}BrN_2OS$: N, 7.23. Found: N, 7.21.

5-Benzal-2,4-thiazoledione (m. p. 243°).[6]—This was obtained in small amounts by the direct hydrolysis of the 5-benzal-2-aryl-2-alkyl compounds, but was also prepared in an interesting way by the action of an excess of sodium hydroxide (40%) on a mixture in hot alcohol of the ethyl *p*-bromophenylthiazolidone and benzaldehyde and precipitating the product with dilute acid.

2-*p*-Bromophenylimino-3-ethyl-4-thiazolidone, $\overline{SC(NC_6H_4Br)NC_2H_5COCH_2}$.—This was isolated from the original ether solution of the ethylation product, remaining in solution after extraction with dilute acid. It formed about one-sixth of the total product, the needles from alcohol melting at 91°.

Anal. Calcd. for $C_{11}H_{11}BrN_2OS$: N, 9.36. Found: N, 9.44.

The same thiazolidone (m. p. 91°) was made by the action of chloroacetyl chloride upon α-ethyl-β-*p*-bromophenyl thiourea in acetone and pyridine solution,[7] thus showing the separate attachment of the ethyl and phenyl groups (N, found, 9.22).

Hydrolysis of this thiazolidone with sulfuric acid gave *p*-bromoaniline and ethylamine, identified by the carbylamine reaction and analysis of its hydrochloride.

2-*p*-Bromophenyl-3-ethyl-5-benzal-4-thiazolidone was made from benzaldehyde and the 91° product from both sources.

Anal. Calcd. for $C_{18}H_{15}BrN_2OS$: N, 7.23. Found: N, 7.21.

On hydrolysis in acid solution it gave *p*-bromoaniline and 3-ethyl-5-benzal-2,4-thiazoledione, melting at 95.5°.

Anal. Calcd. for $C_{12}H_{11}NO_2S$: N, 6.00. Found: N, 5.97.

The formation of the 3-ethyl derivative gives added proof of the structure of the isomeric thiazolidone. Its synthesis from α-ethyl-β-aryl thiourea shows that these thioureas tend to react with the acid chloride in the enol form $C_2H_5NHC(SH)NR$, thus yielding a 3-alkyl-2-aryl-thiazolidone, a fact that has been noted in other cases.

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[6] Andreasch, *Monatsh.*, 10, 75 (1889).

[7] Hunter, *J. Chem. Soc.*, 129, 2955 (1926); Dains, Brewster and Olander, "Organic Syntheses," Vol. VI, p. 72.

The Methylation of the Sodium Salt of *p*-Bromophenylaminothiazolidone.—The same results were obtained both from the use of methyl iodide and of methyl sulfate. The reaction product on extraction with ether left a residue which was soluble in dilute hydrochloric acid and proved to be the 2-methyl-2-*p*-bromophenylaminothiazolidone, prisms from alcohol (m. p. 197°).

Hydrolysis with sulfuric acid (50%) gave ammonia and methyl-*p*-bromophenylamine. This was identified by its reaction with phenyl isocyanate, yielding α-methyl-α-bromophenyl-β-phenyl urea (m. p. 137°) and by the formation of a benzoyl derivative (m. p. 77°). When the 5-benzal compound (m. p. 256° was hydrolyzed it gave the 5-benzal-2,4-thiazoledione (m. p. 242°).

The ether extract from the original methylation product insoluble in dilute acid consisted of the isomeric 2-*p*-bromophenylimino-3-methyl-thiazolidone (m. p. 111°). On hydrolysis methylamine and *p*-bromoaniline were isolated, this proving its constitution. The relative position of the groups was indicated by the hydrolysis of the 5-benzal compound (m. p. 166°) which yielded *p*-bromoaniline and 3-methyl-5-benzal-2,4-thiazoledione (m. p. 133°).

2-Benzyl-2-*p*-bromophenylaminothiazolidone.—This was the only product isolated from the action of benzyl chloride on the sodium salt. It is only slightly soluble in dilute acid. Acid hydrolysis gave ammonia and benzyl-*p*-bromoaniline (m. p. 55°). This was confirmed by a synthetic specimen made from benzyl chloride and *p*-bromoaniline.[8] The fraction of b. p. 237–242° (33 mm.) solidified and melted at 55°.

2-Dibromo-*p*-tolylthiazolidone from 2,6-Dibromo-*p*-toluidine.—This was made by the usual method of refluxing the chloracet derivative with potassium thiocyanate. Methylation of the sodium salt gave nearly equal amounts of the two isomers. The acid soluble 2-methyl-2-dibromo-tolylaminothiazolidone melted at 194°, while the 3-methyl isomer (m. p. 132°) gave a benzal derivative which on hydrolysis yielded the dibromotoluidine, thus proving the structure.

PROPERTIES AND ANALYSES

Thiazolidones	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
2-Methyl-2-*p*-bromophenyl	$C_{10}H_9BrN_2OS$	197	9.82	9.98
5-Benzal-2-methyl-2-*p*-bromophenyl	$C_{17}H_{13}BrN_2OS$	256	7.50	7.52
2-*p*-Bromophenyl-3-methyl	$C_{10}H_9BrN_2OS$	111	9.82	9.88
5-Benzal-2-*p*-bromophenyl-3-methyl	$C_{17}H_{13}BrN_2OS$	166	7.50	7.59
2-Benzyl-2-*p*-bromophenyl	$C_{16}H_{13}BrN_2OS$	153	7.75	7.88
2-Benzyl-2-*p*-chlorophenyl[a]	$C_{16}H_{13}ClN_2OS$	129	8.84	8.77
5-Benzal-2-benzyl-2-*p*-bromophenyl	$C_{23}H_{17}BrN_2OS$	192	6.23	6.38
2-Dibromo-*p*-tolyl	$C_{10}H_8Br_2N_2OS$	250	7.69	7.30
2-Methyl-2-dibromotolyl	$C_{11}H_{10}Br_2N_2OS$	194	7.40	7.68
3-Methyl-2-dibromotolyl	$C_{11}H_{10}Br_2N_2OS$	132	7.40	7.02
2-Ethyl-2-*p*-bromophenyl-5-*o*-chlorobenzal	$C_{18}H_{14}ClBrN_2OS$	192	6.64	6.98
3-Methyl-2,4-diketo-5-benzal	$C_{11}H_9NO_2S$	133	6.39	6.42
5-*o*-Chlorobenzal-diketo[b]	$C_{10}H_6ClNO_2S$	172	5.84	5.86
Other Derivatives				
α-Methyl-α-*p*-bromophenyl-β-phenyl urea	$C_{14}H_{12}BrNO$	77	4.96	4.54
Benzyl-*p*-bromoaniline	$C_{13}H_{12}BrN$	55	5.34	5.21
ω-Chloracet-dibromo-*p*-toluide	$C_9H_8Br_2ClNO$	184	4.09	4.06

[a] This *p*-chlorophenyl thiazolidone gave only the 2-benzyl isomer. [b] From the hydrolysis of *o*-chlorobenzal derivative of the 2-ethyl-2-*p*-bromophenyl thiazolidone.

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(8) "Organic Syntheses," Vol. VIII, p. 38.

Summary

The aryl thiazolidones studied correspond to the 2-arylamino or stable forms of Wheeler and Johnson.

Their sodium salts with methyl or ethyl iodide yield a mixture of 2-alkyl-2-aryl and of 3-alkyl-2-aryl thiazolidones. With benzyl chloride only the 2-benzyl derivative has been found.

These results have failed to confirm the formulation of Beckurts and Frerich, who assumed that the products they obtained were 2-alkylimino-3-aryl thiazolidones. Further unpublished investigations in this Laboratory support our experimental results.

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The Catalytic Hydrogenation of the Halogenomorphides: Dihydrodesoxymorphine-D[1]

BY LYNDON F. SMALL, KECHEE C. YUEN AND LOUIS K. EILERS

In a previous paper from this Laboratory[2] it was shown that catalytic hydrogenation of the halogenocodides yielded, according to the conditions, varying amounts of three hydrogenated desoxycodeine derivatives. By empirical selection of the proper catalyst and solvent, it was possible to direct the hydrogenation in such a way that the non-phenolic dihydrodesoxycodeine-D (IV) was the principal product obtained from any of the four known halogenocodides. Dihydrodesoxycodeine-D,[3] and its unsaturated analog, desoxycodeine-C (II),[4] in both of which the 4,5-ether bridge is still intact, are of particular interest pharmacologically, since they differ structurally from certain codeine derivatives (dihydrocodeine and pseudocodeine, respectively) only in having a hydrogen atom in place of the alcoholic hydroxyl of the codeine series. The demethylated analog of desoxycodeine-C, namely, desoxymorphine-C (I), which may be regarded as a derivative of γ-isomorphine, has already been described,[5] and has been found extraordinarily active in the animal body. With the view of preparing a dihydrodesoxymorphine of the dihydrodesoxycodeine-D type, corresponding in fundamental structure to dihydromorphine (Paramorfan), the catalytic hydrogenation of the halogenomorphides has been investigated.

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(1) This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc., and the Rockefeller Foundation.

(2) Mosettig, Cohen and Small, THIS JOURNAL, 54, 793 (1932).

(3) Small and Cohen, *ibid.*, 53, 2227 (1931).

(4) Small and Cohen, *ibid.*, 53, 2214 (1931).

(5) Small and Morris, *ibid.*, 55, 2874 (1933).

The three known halogenomorphides, on catalytic hydrogenation under identical conditions, yield varying amounts of three different products. α-Chloromorphide, in methyl alcoholic or weakly acid solution, gives largely the desired dihydrodesoxymorphine-D (III), together with some tetrahydrodesoxymorphine and a little non-crystalline material. In the case of β-chloromorphide, the product is almost exclusively dihydrodesoxymorphine-D. Bromomorphide which is believed (without good evidence) to correspond in structure to β-chloromorphide, yields, on the other hand, only small amounts of dihydrodesoxymorphine-D and a large quantity (up to 70%) of an uncrystallizable oil. This oil could not be distilled in high vacuum at any reasonable temperature, which led us to believe that it might correspond in structure to bis-dihydrodesoxycodeine. Decisive chemical evidence on this point could not be obtained, for the product resulting from methylation of the oil gave only one methiodide (amorphous), containing one atom of iodine to one molecule of desoxycodeine base; this does not necessarily exclude a dimolecular structure. An attempt to prepare a bis-dihydrodesoxymorphine for comparison, by demethylation of bis-dihydrodesoxycodeine with hydriodic acid, resulted in a phenolic base containing iodine.

The discrepancy between the hydrogenation of β-chloromorphide and that of bromomorphide has its parallel in a similar observation in the halogenocodide series, but does not permit of any valid conclusion concerning the structure of the two halogenomorphides, since the mechanism of the hydrogenation of these halogeno derivatives is uncertain.[6] The change in reduction conditions, from base in organic solvent to the salt in dilute acid solution, does not produce as great an effect on the course of hydrogenation as was observed in the halogenocodide series. For the halogenomorphides, faintly acid solution increases somewhat the yield of tetrahydrodesoxymorphine, and decreases the amount of oily product formed. In the case of the halogenocodides, good yields of dihydrodesoxycodeine-D could be obtained only by hydrogenation in acid solution, and in alcohol tetrahydro-

TABLE I

CATALYTIC HYDROGENATION OF THE HALOGENOMORPHIDES

(Palladium on Barium Sulfate as Catalyst)

Substance	Solvent	Moles H_2	Dihydrodesoxy-morphine-D, %	Tetra-hydrodesoxy-morphine, %	Oil, %
α-Chloromorphide	Methanol	1.86	70	11[a]	19
α-Chloromorphide	Dil. HCl	2.27	56	33	11
β-Chloromorphide	Methanol	2.0	100	..	..
β-Chloromorphide	Dil. HCl	2.28	83	17	..
Bromomorphide	Methanol	1.86	30	a	70
Bromomorphide	Dil. HCl	1.87	63	5	32

[a] Trace of unidentified base of m. p. 275–277°.

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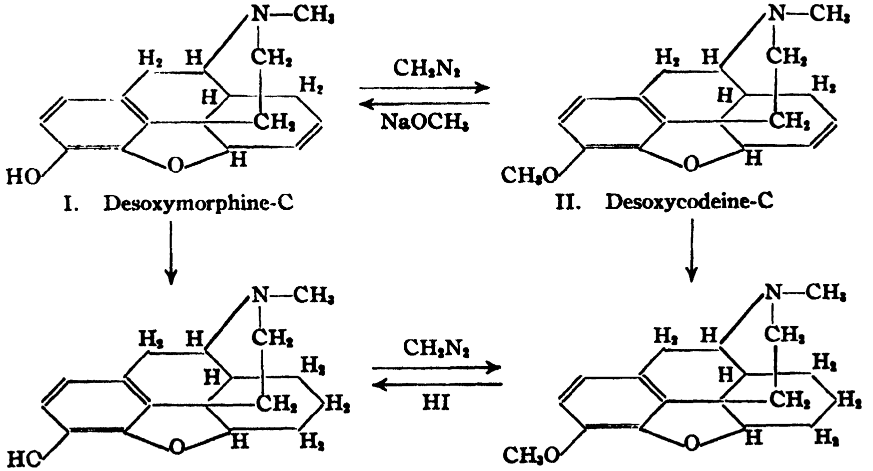
(6) Ref. 2, p. 795.

desoxycodeine or bis-dihydrodesoxycodeine resulted almost exclusively. In a repetition of some of the experiments of Mosettig, Cohen and Small, however, we have found that the results of hydrogenation often depend upon unrecognizable slight differences in catalyst or conditions, so that the discrepancy between the morphide and codide series may be largely illusory.

Dihydrodesoxymorphine-D, the principal product from the hydrogenation of α- and β-chloromorphides, is a colorless, well-crystallized base of m. p. 188–189°. It occurs also in a hemihydrated form of lower melting point, which can be converted to the anhydrous form by sublimation in high vacuum. It is not the same as the "dihydrodesoxymorphine" (m. p. 183°) of Knoll and Co.,[7] for the latter is beyond doubt identical with desoxymorphine-C (m. p. 189–190°).[8] The structure of dihydrodesoxymorphine-D is evident from its methylation, which leads to the non-phenolic dihydrodesoxycodeine-D (IV). Furthermore, dihydrodesoxymorphine-D can be obtained as the hydriodide in 93% yield from demethylation of dihydrodesoxycodeine-D. In view of the difficulty of preparation of the halogenomorphides, this constitutes the most practicable preparative method, for dihydrodesoxycodeine-D can be made quantitatively from the easily accessible α-chlorocodide. Dihydrodesoxymorphine-D can also be prepared by "normal" reduction of desoxymorphine-C under the special conditions developed by Lutz and Small[9] for partial hydrogenation of pseudocodeine types.



I. Desoxymorphine-C

II. Desoxycodeine-C

III. Dihydrodesoxymorphine-D

IV. Dihydrodesoxycodeine-D

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(7) Knoll and Co., German Patent 414,598 (1922); *Friedländer*, 15, 1518; *Jahresber. Chem. Tech.*, 71, 123 (1925).

(8) Small and Morris, THIS JOURNAL, 55, 2876 (1933). Although desoxymorphine-C and dihydrodesoxymorphine-D show the same melting point, an identity of these two substances does not come into question, for they differ in other physical properties, and give a mixed melting point depression of 15°. Moreover, desoxymorphine-C can be hydrogenated with extreme ease, while dihydrodesoxymorphine-D is indifferent to catalytic hydrogenation.

(9) Lutz and Small, *ibid.*, 54, 4715 (1932).

In contrast to its dihydrodesoxycodeine analog, dihydrodesoxymorphine-D is unaffected by prolonged electrolytic reduction. The same unexpected difference in reactivity toward electrolytic reduction has already been noted in the cases of desoxycodeine-C and desoxymorphine-C. It may depend upon imperceptible differences in conditions, and will be the subject of further study.

Because of the differences shown by β-chloromorphide and bromomorphide in catalytic hydrogenation, the electrolytic reduction of bromomorphide was investigated. It proceeds in the same way as that of α-chloromorphide, and yields desoxymorphine-A in 79% of the calculated amount. The reduction of α-chloromorphide with amalgamated zinc and 6-normal hydrochloric acid gives a good yield of a mixture of β-isomorphine (evidently formed by hydrolysis of the α-chloromorphide) and desoxymorphine-A. Bromomorphide yields the same products.

As a result of further attempts to verify the existence of a desoxymorphine which Schryver and Lees[10] prepared by treatment of α-chloromorphide with tin and hot concentrated hydrochloric acid, we have obtained minute quantities of an alkaloid hydrochloride of m. p. 262° and $[\alpha]_D$ −78°. The same product results from heating α-chloromorphide with stannous chloride and concentrated hydrochloric acid under pressure at 100°. The new hydrochloride is not the same as that of Schryver and Lees, for which the specific rotation +140.3° was given, nor does it correspond to any of the known desoxymorphine derivatives. It seems to us questionable whether the morphine carbon–nitrogen skeleton would withstand such drastic acid treatment without undergoing fundamental structural changes, since even in the preparation of β-chloromorphide from morphine and hydrochloric acid, a considerable part of the material is converted into apomorphine.

The physiological action of dihydrodesoxymorphine-D has been studied by Dr. N. B. Eddy at the Pharmacological Laboratory of the University of Michigan and will be described in detail in a publication from that Institution. In agreement with the change in physiological action which we have observed to result from replacement of the alcoholic hydroxyl group of the morphine and codeine series by hydrogen, dihydrodesoxymorphine-D is more active than dihydromorphine. Its toxicity is about the same as that of dihydromorphine, but respiratory and analgesic effects are greater. Dihydrodesoxymorphine-D likewise shows more analgesic action than its other hydroxy analog, dihydro-γ-isomorphine.[11]

Experimental

Hydrogenation of α-Chloromorphide.—The α-chloromorphide used in these experi-

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(10) Schryver and Lees, *J. Chem. Soc.*, **77**, 1024 (1900).

(11) This new derivative of the morphine isomers has been prepared by hydrogenation of γ-isomorphine under special conditions, as well as by demethylation of the non-phenolic dihydropseudocodeine, and will be described in a later paper from this Laboratory.

ments was prepared by treatment of morphine with thionyl chloride,[12] and was purified by dissolving in dilute hydrochloric acid, precipitating with sodium carbonate and extracting the amorphous precipitate rapidly into ether. After several repetitions of this process, the crystalline material from the ether was washed with cold alcohol, which removed a considerable amount of another halogeno compound. The purified material showed $[\alpha]_D$ −363.6° (methanol, c = 0.528). Insufficiently pure chloromorphide leads to very complex hydrogenation mixtures.

Fifteen grams of α-chloromorphide dissolved in 150 cc. of absolute methanol was hydrogenated in the presence of 1.04 g. of palladium–barium sulfate (= 0.05 g. Pd metal). The absorption amounted to 2064 cc. of hydrogen, most of which was taken up in the first three hours, total time, eleven hours. The solution was freed of colloidal palladium by filtering through a layer of Norit, and the methanol removed at 40° in vacuum with a bubble-tube. The colorless resin which resulted was taken up in 100 cc. of water, and the alkaloid precipitated out by slow addition of ammonia, shaking into ether after each addition. Toward the end, the separation of crystalline tetrahydrodesoxymorphine caused troublesome emulsions. The ether was distilled down to 100 cc., and the crystalline tetrahydrodesoxymorphine, with a little dihydrodesoxymorphine-D, was filtered out. After washing with acetone to remove dihydrodesoxymorphine-D (0.6 g.) the tetrahydro product (together with that filtered off during the extraction) weighed 1.5 g. It had the m. p. 228–230°, and was identified by conversion to tetrahydrodesoxycodeine with diazomethane.

The ether solution from which the tetrahydrodesoxymorphine had been separated was distilled down to a yellow oil, which crystallized on rubbing with ethyl acetate. The crystals (3.6 g.) melted at 172–184°, and were purified from ethyl acetate; during this process, 60 mg. of a sparingly soluble base, m. p. 272–276°, was isolated. Analysis of this high-melting base gave the values C, 74.47; H, 7.53. It gave on methylation a colorless oil. The ethyl acetate mother liquors from the main portion gave on further evaporation 5 g. of a base of m. p. 155–170° which proved to be dihydrodesoxymorphine-D hemihydrate. The total yield of dihydrodesoxymorphine-D was 9.2 g.

As an alternative procedure, which is advantageous when much oily material is present, the residue from ether distillation may be extracted with cold acetone, the latter distilled to dryness and the residue treated with absolute alcoholic oxalic acid. Dihydrodesoxymorphine-D acid oxalate crystallizes well even in the presence of large amounts of impurities.

Dihydrodesoxymorphine-D.—Anhydrous dihydrodesoxymorphine-D melts at 188–189°, and has the specific rotation in absolute methanol $[\alpha]^{28}_D$ −76.8° (c = 1.614).

Anal. Calcd. for $C_{17}H_{21}O_2N$: C, 75.23; H, 7.81. Found: C, 74.82, 74.91; H, 7.85, 7.96.

Dihydrodesoxymorphine-D crystallizes best from acetone or ethyl acetate; in alcohol solution it turns red rapidly. It is precipitated by addition of water to its solution in acetone in the form of regular rectangular plates. It sublimes between 140 and 170° at 0.001 mm. pressure. The alkaloid behaves abnormally in camphor: The mixture shows two melting points, 133.5 and 166°, and on cooling, two solidification points, at about the same temperatures.

Two grams of dihydrodesoxymorphine-D in 200 cc. of 20% sulfuric acid was reduced electrolytically at 6 amp. on a 60 sq. cm. electrode for five hours at 10°, and for four more hours at 25°. The starting material, 1.8 g., was regained: m. p. 188–189°, $[\alpha]^{27}_D$ −75.3°.

Dihydrodesoxymorphine-D, 1.3 g., in ethereal solution with a few cc. of methanol was allowed to react with 0.2 g. of diazomethane for twenty-four hours. The yield of crude crystalline methylation product was nearly quantitative. After purification from acetone it had the m. p. 106–107° of dihydrodesoxycodeine-D, and showed $[\alpha]^{20}_{D}$ −81.3° in alcohol.

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[12] Wieland and Kappelmeier, *Ann.*, **382**, 306 (1911).

Demethylation of Dihydrodesoxycodeine-D.—A solution of 15 g. of dihydrodesoxycodeine-D in 45 cc. of hydriodic acid, sp. gr. 1.7, was boiled vigorously for three minutes. To the cooled solution, water (about 150 cc.) was added slowly with scratching until crystals no longer separated. The mixture was warmed nearly to boiling, whereby the crystals became pure white and more granular. The yield of dihydrodesoxymorphine-D hydriodide was 17.3 g. From the mother liquor an additional 1.5 g. of pure dihydrodesoxymorphine-D base was obtained by precipitation with ammonia.

TABLE II

DIHYDRODESOXYMORPHINE-D DERIVATIVES

Derivative	$[\alpha]_D$, solvent, c, t°C	Formula	Analyses, % Calcd.		Found	Calcd.		Found
Hydriodide[a]	−48.4°, water, 1.650,25	$C_{17}H_{21}O_2N \cdot HI$	I,	31.81	32.19	....		....
Hydrochloride[b]	−66.8°, water, 0.898,27	$C_{17}H_{21}O_2N \cdot HCl$	Cl,	11.53	11.54	....		....
Sulfate[c]	−57.9°, water, 1.425,29	$(C_{17}H_{21}O_2N)_2H_2SO_4 + 2H_2O$	H_2O	5.32	5.33	SO_4,	14.99[d]	15.20[d]
Acid oxalate[e]	−57.9°, water, 1.659,28	$C_{19}H_{23}O_6N$	C,	63.12	62.87	H,	6.42	6.43
Salicylate[f]	−42.8°, alc., 0.794,28	$C_{24}H_{27}O_5N$	C,	70.38	69.93	H,	6.64	6.94
Methiodide[g]	−46.6°, water, 1.009,27	$C_{18}H_{24}O_2NI$	C,	52.29	52.26	H,	5.86	5.98

[a] Best purified from water; 100 g. satd. aqueous solution at 25° contains 3.86 g. of the salt. [b] Prepd. from base with alcoholic hydrochloric acid, purified from 95% alcohol; exceedingly soluble in water. [c] Prepd. from base with sufficient cold 10% sulfuric acid to turn Congo paper; salt is sparingly soluble in cold water, very soluble in hot water, and is best suited to purification of the alkaloid. Colors slightly at 210°, unmelted at 230°. [d] Anhydrous salt, $(C_{17}H_{21}O_2N)_2H_2SO_4$. [e] Prepd. from base with absol. alcoholic oxalic acid; sparingly sol. in alcohol, very sol. in water, recryst. from 50% alcohol. [f] Prepd. in absolute alcohol with alcoholic salicylic acid, recryst. from 95% alcohol. Different preparations of the salt did not give consistent analyses; under some conditions it apparently crystallizes with a variable amount of water. [g] Prepd. by adding excess methyl iodide to suspension of the alkaloid in hot acetone; the amorphous methiodide becomes cryst. on further heating, and can be recryst. from alcohol.

Dihydrodesoxymorphine-D Hemihydrate.—This derivative was obtained as one of the products from most of the hydrogenations of the halogenomorphides, and usually separated from the ethyl acetate solution which had already yielded a crop of the anhydrous base. The conditions which determine its formation are not known; we were never able to obtain the hemihydrate from the anhydrous base. The hemihydrate does not lose its hydrate water in high vacuum below the temperature at which sublimation occurs, and a direct determination of hydrate water was not possible. The hemihydrate melts at 162–164° with gas evolution, and has $[\alpha]^{28}_{D}$ −78.6° (ethyl acetate, c = 1.076). It gives the anhydrous base of m. p. 188–189° quantitatively on sublimation. Its salts are identical with those of the anhydrous base, and it gives by methylation dihydrodesoxycodeine-D (70% yield).

Anal. Calcd. for $C_{17}H_{21}O_2N + 0.5H_2O$: C, 72.85; H, 7.93. Found: C, 72.85; H, 8.11.

Dihydrodesoxymorphine-D from Desoxymorphine-C.—A suspension of 2.27 g. of finely powdered desoxymorphine-C hydrochloride (= 2.00 g. of alkaloid) in 15 cc. of glacial acetic acid absorbed 266 cc. (= 1.4 moles) of hydrogen in the presence of 0.05 g. of platinum oxide. The product was precipitated with ammonia, extracted into ether, and the residue from distillation of the ether rubbed up with acetone. The acetone-insoluble tetrahydrodesoxymorphine, 0.75 g., was converted to the salicylate, which melted at 232° and had $[\alpha]^{25}_{D}$ −31.6°. The acetone extract yielded 0.75 g. of dihydrodesoxymorphine-D, which after one crystallization from acetone melted at 185–186° and had $[\alpha]^{25}_{D}$ −84.6°.

Hydrogenation of α-Chloromorphide in Acid Solution.—Five grams of α-chloromorphide suspended in 100 cc. of water was brought into solution by addition of normal hydrochloric acid and hydrogenated in the presence of 1.05 g. of palladium–barium sulfate. The absorption amounted to 2.27 moles of hydrogen most of which was taken up in the first hour. By precipitation with ammonia and extraction with ether, 1.5 g. of dihydrodesoxymorphine-D hemihydrate was obtained, and 1.5 g. of the ether-insoluble tetrahydrodesoxymorphine. The aqueous layer gave a heavy Mayer's test, and yielded on further extraction 1.0 g. of anhydrous dihydrodesoxymorphine-D.

Hydrogenation of β-Chloromorphide.—The β-chloromorphide used was prepared by the action of fuming hydrochloric acid on morphine at 100°[13] and was purified most advantageously as the tartrate, $[\alpha]^{25}_{D}$ +7.4° (water, c = 2.708). The base liberated from the tartrate had $[\alpha]^{25}_{D}$ −4° (methanol, c = 2.115) and melted at about 182°. Hydrogenation of 5.34 g. of β-chloromorphide in 100 cc. of methanol in the presence of Pd–$BaSO_4$ resulted in absorption of 2 moles of hydrogen in about two hours. The product, isolated as described for α-chloromorphide, consisted of 4.5 g. of colorless crystals of dihydrodesoxymorphine-D. By crystallization from ethyl acetate, 3 g. of anhydrous base was obtained, and from the ethyl acetate mother liquors 1.5 g. of the hemihydrate.

When the hydrogenation was carried out in dilute hydrochloric acid solution, the hemihydrate form only, of dihydrodesoxymorphine-D, with about 17% of tetrahydrodesoxymorphine, was obtained.

Hydrogenation of Bromomorphide.—Bromomorphide was prepared by the method of Schryver and Lees[14] and purified from methanol. It sintered and darkened at 164°, and melted above 200°. In methanol it showed $[\alpha]^{28}_{D}$ +73.9° (c = 2.788). When bromomorphide was hydrogenated in methanol, with Pd–$BaSO_4$, 4.85 g. of alkaloid took up 1.86 moles of hydrogen, and yielded 1.0 g. of dihydrodesoxymorphine-D hemihydrate. The remaining material was a viscous oil, containing a trace of the high-melting base mentioned under α-chloromorphide. The oil did not give a crystalline ether on treatment with diazomethane. The methylation product in benzene with methyl iodide gave a methiodide of m. p. 235–238°, which appeared to be amorphous, and could be purified only by washing with acetone. It was not the monomethiodide of a dimolecular base, for analysis showed 29.51% iodine, and its properties were not those of bis-dihydrodesoxycodeine dimethiodide. The hydrogenation of bromomorphide in methanol with platinum oxide gave only a small amount of crystalline product, which proved to be tetrahydrodesoxymorphine.

Hydrogenation of bromomorphide in dilute hydrochloric acid gives more crystalline material than in methanol. From 4.85 g. of bromomorphide, absorption of 1.87 moles of hydrogen, 2.4 g. of dihydrodesoxymorphine-D hemihydrate, 0.2 g. of tetrahydrodesoxymorphine, and 1.2 g. of uncrystallizable oil were obtained.

Electrolytic Reduction of Bromomorphide. Desoxymorphine-A.—Six grams of bromomorphide in 250 cc. of 20% sulfuric acid was reduced at 20° with 12 amp. on a 60 sq. cm. lead cathode, time seven hours. A trace of sodium hydrosulfite was added, the base precipitated out with ammonia, and extracted several times with ether. The calculated amount of salicylic acid was added to the dried ether solution, which was then concentrated to 100 cc. A yield of 4.5 g. (79%) of desoxymorphine-A salicylate was obtained. After purification from alcohol it melted at 248–250° (gas evolution)

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(13) Ach and Steinbock, *Ber.*, **40**, 4282 (1907).

(14) Schryver and Lees, *J. Chem. Soc.*, **77**, 1032 (1900).

and had $[\alpha]^{25}_{D}$ +93.6° (methanol, c = 0.801). The base prepared from the salicylate melted at 257–258° with decomp.

Reduction of α-Chloromorphide and Bromomorphide with Zinc.—Fifty grams of α-chloromorphide in 1 liter of 6 N hydrochloric acid was heated at 60° for fourteen hours with 100 g. of amalgamated zinc. After eight days further reaction at room temperature, the solution was treated with excess concd. ammonia, and the precipitated alkaloid extracted into ether. The aqueous layer contained much β-isomorphine, which was isolated by exhaustive extraction with ether, and characterized as the salicylate. The main ether extract was heated with 25 g. of salicylic acid and distilled. Twenty grams of a crystalline salicylate was obtained, m. p. 164–178°, which after repeated crystallizations from alcohol showed the constant m. p. 204–206°, $[\alpha]^{27}_{D}$ −53° (methanol, c = 0.849). Analysis indicated that this was a mixture of a desoxymorphine salicylate and the salicylate of one or more of the morphine isomers. By converting the mixed salicylate back to the alkaloid, desoxymorphine-A of m. p. 258° could be isolated; it did not depress the m. p. of a known sample.

Anal. Calcd. for $C_{17}H_{19}O_2N$: C, 75.80; H, 7.11. Found: C, 75.92; H, 7.15.

Reduction of bromomorphide in the same way gave the same mixture of salicylates.

Reduction of α-Chloromorphide with Tin.—When α-chloromorphide was reduced with tin and concd. hydrochloric acid as described by Schryver and Lees, 3% yield of a crystalline hydrochloride was obtained by allowing an alcoholic solution of the oily hydrochloride to stand for several weeks. It was difficultly soluble in alcohol and could be recrystallized from water. It melted sharply at 263.5° with decompn. and showed $[\alpha]^{27}_{D}$ −78.1° in water (c = 1.050). The hydrochloride of Lees had the rotation $[\alpha]_{D}$ +140.3°. The same hydrochloride (5% yield) was obtained when α-chloromorphide was reduced with stannous chloride and concd. hydrochloric acid under pressure at 100°. It was impossible to purify it to the point where it did not leave a trace of inorganic material on combustion.

Anal. Found: C, 58.73; H, 6.74.

The alkaloid liberated from this hydrochloride could not be obtained crystalline, and gave only a colorless oil on methylation.

Summary

1. Catalytic hydrogenation of the three known halogenomorphides results in varying amounts of dihydrodesoxymorphine-D, tetrahydrodesoxymorphine and an unidentified oil.

2. Dihydrodesoxymorphine-D is obtained in nearly quantitative yield by demethylation of dihydrodesoxycodeine-D. It may likewise be prepared by controlled hydrogenation of desoxymorphine-C.

3. Electrolytic reduction of bromomorphide yields chiefly desoxymorphine-A. Reduction of α-chloromorphide or bromomorphide with zinc and hydrochloric acid gives desoxymorphine-A, β-isomorphine and probably other of the morphine isomers.

UNIVERSITY, VIRGINIA

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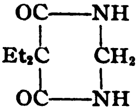
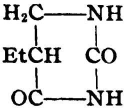
Homodesoxyveronal and Some of its Homologs

BY ARTHUR W. DOX

By electrolytic reduction of veronal (barbital) Tafel and Thompson[1] obtained a diethyldiketohexahydropyrimidine (I) which they designated desoxyveronal. Hydrolysis of this product, whereby diethylmalonic acid was obtained, showed that the reduction had occurred in the urea carbonyl. When, however, the corresponding monoethylbarbituric acid was electrolyzed in the same manner, the reduction occurred in one or both of the malonyl carbonyls, depending on temperature and current density, yielding ethylhydrouracil (II) or ethyltrimethyleneurea (III).


I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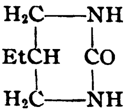
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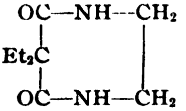
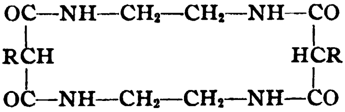
Desoxyveronal (I) may be regarded as a cyclic amide of a dibasic acid, the ring closure being effected by substitution of methylene. It should be possible to prepare the substance by direct condensation of diethylmalonyl chloride with methylenediamine. From the high melting point (292°) of desoxyveronal, however, together with the fact that no further study was made, the inference seems warranted that the unrecorded pharmacological tests failed to reveal hypnotic action.[2]

The homologous seven-membered structure, which may be designated homodesoxyveronal (IV), was considered of sufficient interest in this connection to make desirable its preparation and examination. Such a structure should result by condensation of the chloride or ester of diethylmalonic acid with ethylenediamine. Since the esters of malonic acids are more readily available than the chlorides, they were used in the present experiments. The condensations were effected by heating molecular proportions of ester and amine for six to eight hours at 100–110° with absolute alcohol in which two equivalents of sodium had been dissolved. In place of the free base the hydrochloride was also used successfully, with two additional equivalents of sodium ethoxide to liberate the base. Both


IV


V

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[1] Tafel and Thompson, *Ber.*, **40**, 4489 (1907).

[2] Desoxyveronal was also prepared by Einhorn [*Ann.*, **359**, 176 (1908)] by sodium reduction of veronal, but he likewise omits mention of its pharmacological properties.

procedures gave the same condensation products and in practically the same yields. In all, six esters were used, three of dialkyl- and three of monoalkyl-malonic acids. Analyses of the products gave values in satisfactory agreement with those calculated for the seven-membered ring structures.

TABLE I

HOMODESOXYBARBITURIC ACIDS

			Found, %			Calcd., %		
Dialkyl	Formula	M. p., °C.	C	H	N	C	H	N
Diethyl	$C_9H_{16}N_2O_2$	306	58.22	8.71	15.31	58.69	8.70	15.22
Dibutyl	$C_{13}H_{24}N_2O_2$	290	64.42	10.30	11.51	65.00	10.00	11.67
Hexylethyl	$C_{13}H_{24}N_2O_2$	188	65.16	10.21	11.47	65.00	10.00	11.67
Monoalkyl		(decompn.)						
Ethyl	$C_7H_{12}N_2O_2$	350–355	53.25	7.74	17.47	53.85	7.69	17.95
Propyl	$C_8H_{14}N_2O_2$	242–245	55.22	8.45	16.53	56.47	8.24	16.47
Sec-butyl	$C_9H_{16}N_2O_2$	335–340	57.48	8.75	14.78	58.69	8.70	15.22

Dialkyl-homodesoxybarbituric Acids.—A striking difference was at once apparent between the dialkyl and the monoalkyl derivatives. The former are well-defined crystalline products, but obtained in rather poor yield. They have high, but sharp melting points; on cooling, the melt rapidly solidifies in crystals which show the same melting point as before. Recrystallization is readily effected by cooling or diluting the alcoholic solution. The diethyl derivative has a slightly bitter taste, the two homologs are tasteless. In contrast to desoxyveronal they are insoluble in alkali.

Monoalkyl-homodesoxybarbituric Acids.—These were obtained in much better yields but were invariably amorphous and could not be crystallized from any of the solvents tried. They dissolve in hot glacial acetic acid, but separate as an amorphous slime when the solution is chilled or allowed to evaporate spontaneously. They show a strong tendency to swell to a semi-gelatinous mass in water and for that reason are difficult to filter and purify. Dry powders free from ash were eventually obtained by successive treatments with alcohol and ether. The melting points are high but not sharp and decomposition occurs with darkening in color and evolution of gas. The amorphous character of these products suggests a polymeric structure such as might be represented by Formula V.

The difference in behavior of the esters of dialkyl- and monoalkyl-malonic acids in the condensation with ethylenediamine is not surprising in view of a somewhat similar difference in their reaction with hydrazine.[3] The product there consisted of a single pyrazole ring or the double pyrazopyrazole ring, depending on the absence or presence of an unsubstituted hydrogen in the malonyl grouping. Differences also in reactivity toward ammonia to form amides have long been known.[4]

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(3) Dox, THIS JOURNAL, 54, 3674 (1932).

(4) Fischer and Dilthey, *Ber.*, 35, 884 (1902).

Homodesoxybarbituric Acid.—A reaction between ethyl malonate and ethylenediamine is mentioned in the older literature. Freund[5] obtained an "ethylenemalonamide" by direct condensation without solvent or catalyst. The same substance was again obtained by Ruhemann and Sedzwick[6] as a by-product in the reaction between ethyl dicarboxyglutaconate and ethylenediamine. Aside from the statement that the substance is readily soluble in water, precipitated by alcohol, and melts with decomposition at 280°, nothing is said of its properties.

The writer prepared this ethylenemalonamide (homodesoxybarbituric acid) by the Freund reaction and obtained an amorphous polymeric substance which melted at 280° with decomposition. Its aqueous solution was distinctly colloidal. For example, the warm solution is water clear; on cooling it becomes opaque, but clears up again on warming. In the direct condensation, without solvent or catalyst, between a malonic ester and ethylenediamine, the effect of alkyl substitution in the former is rather striking. Ethyl malonate and the amine react at once with a very considerable rise in temperature, and in a few moments the mixture sets to an opaque gel containing the amorphous condensation product. Ethyl ethylmalonate and the amine form a homogeneous solution but no reaction occurs even after twenty-four hours of standing. When the solution is heated in the steam-bath a white precipitate gradually forms and the mass eventually becomes gelatinous. Ethyl diethylmalonate, on the other hand, does not react with ethylenediamine even after several hours of heating.

As might be expected from the properties of homodesoxyveronal and its higher homologs, these derivatives were found to be pharmacologically inert. Administered orally to rabbits in doses equivalent to the hypnotic dose of barbital no effect whatever was observed.

Summary

Homodesoxyveronal, the seven-membered heterocycle homologous to desoxyveronal, has been synthesized by condensation of ethyl diethylmalonate and ethylenediamine. Its dibutyl and hexylethyl homologs have also been obtained by the same procedure.

Esters of monoalkylmalonic acids also condense with ethylenediamine, yielding products with empirical formulas corresponding to the seven-membered homodesoxybarbituric acids. These products, however, are amorphous and colloidal in character and probably have a polymeric structure.

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[5] Freund, *Ber.*, 17, 137 (1884).

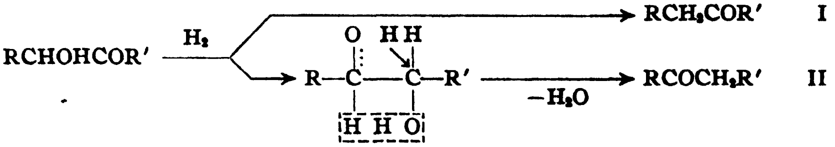
[6] Ruhemann and Sedzwick, *ibid.*, 28, 824 (1895).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Benzoin Reduction. II. The Mechanism of Ketone Formation. The Case of *m*-Chlorobenzanisoin

BY SANFORD S. JENKINS AND EDWIN M. RICHARDSON

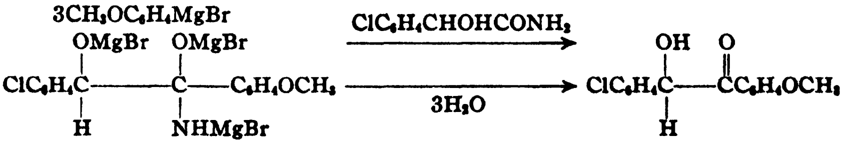
It has been shown previously[1] that certain unsymmetrical benzoins produce *two isomeric* desoxybenzoins when reduced with tin and hydrochloric acid in alcoholic solution and the results obtained were explained by the equations



$$RCHOHCOR' \xrightarrow{H_2} \begin{cases} \longrightarrow RCH_2COR' & \text{I} \\ R-\overset{O}{\underset{H}{C}}-\overset{HH}{\underset{O}{C}}-R' \xrightarrow{-H_2O} RCOCH_2R' & \text{II} \end{cases}$$

This explanation was justified by the fact that the glycol when prepared independently and dehydrated, invariably produced the ketone corresponding to reaction II to the exclusion of I.

The object of the present article is to describe the results which were obtained in the reduction, under similar conditions, of *m*-chlorobenzanisoin in order to test further the validity of the above explanation. This benzoin, which has not been described previously, was prepared in the usual manner by condensing *m*-chlorobenzaldehyde and anisaldehyde in the presence of potassium cyanide. It was shown to be *m*-chloro-α-hydroxybenzyl *p*-methoxyphenyl ketone by comparison with this substance as obtained by reacting *m*-chloromandelamide[2] with *p*-methoxyphenylmagnesium bromide according to the equations



$$3CH_3OC_6H_4MgBr \xrightarrow{ClC_6H_4CHOHCONH_2}$$

$$ClC_6H_4\overset{OMgBr}{\underset{H}{C}}-\overset{OMgBr}{\underset{NHMgBr}{C}}-C_6H_4OCH_3 \xrightarrow{3H_2O} ClC_6H_4\overset{OH}{\underset{H}{C}}-\overset{O}{\overset{\parallel}{C}}C_6H_4OCH_3$$

When oxidized with Fehling's solution the benzoin produced the benzil and when reduced with sodium amalgam *sym*-*m*-chloro-*p*′-methoxydiphenylethylene glycol was obtained. The glycol was dehydrated by heating with a solution consisting of 10% concd. sulfuric acid in glacial acetic acid and *p*-methoxybenzyl *m*-chlorophenyl ketone was isolated. The filtrate was carefully examined for the isomeric ketone but only intractable gum could be separated. That the ketone actually has the structure assigned was shown by comparison with the substance as obtained by condensing *p*-methoxyphenylacetamide with *m*-chlorophenylmagnesium iodide according to the reactions

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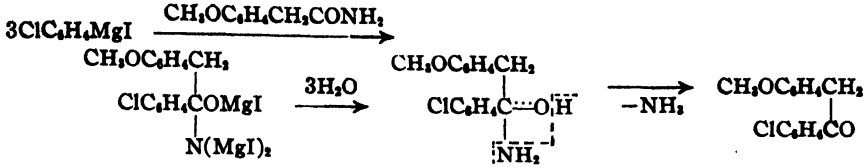
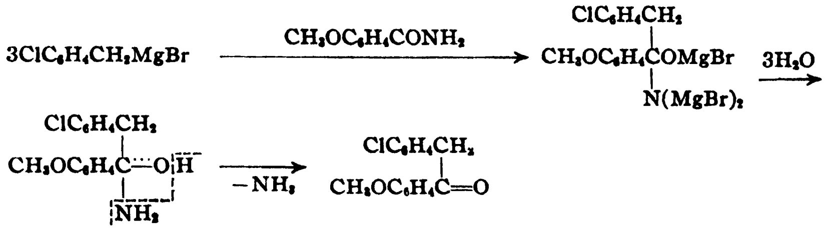
(1) Jenkins, THIS JOURNAL, 54, 1153 (1932).

(2) Jenkins, *ibid.*, 53, 2341 (1931).



$$3\,ClC_6H_4MgI \xrightarrow{CH_3OC_6H_4CH_2CONH_2} \underset{\textstyle N(MgI)_2}{\overset{\textstyle CH_3OC_6H_4CH_2}{ClC_6H_4COMgI}} \xrightarrow{3H_2O} \underset{\textstyle NH_2}{\overset{\textstyle CH_3OC_6H_4CH_2}{ClC_6H_4C{-}OH}} \xrightarrow[-NH_3]{} \overset{\textstyle CH_3OC_6H_4CH_2}{ClC_6H_4CO}$$

and also by converting it into the oxime, which was rearranged in the Beckmann manner[3] to *p*-methoxyphenylaceto-*m*-chloroanilide the structure of which was established by comparison with an authentic sample (see experimental part). The isomeric ketone, which is *m*-chlorobenzyl *p*-methoxyphenyl ketone, was also prepared independently by condensing *m*-chlorobenzyl bromide[4] with *p*-methoxybenzamide according to the method of synthesizing desoxybenzoins which has been described previously.[5] The reactions may be represented as



$$3\,ClC_6H_4CH_2MgBr \xrightarrow{CH_3OC_6H_4CONH_2} \underset{\textstyle N(MgBr)_2}{\overset{\textstyle ClC_6H_4CH_2}{CH_3OC_6H_4COMgBr}} \xrightarrow{3H_2O} \underset{\textstyle NH_2}{\overset{\textstyle ClC_6H_4CH_2}{CH_3OC_6H_4C{-}OH}} \xrightarrow[-NH_3]{} \overset{\textstyle ClC_6H_4CH_2}{CH_3OC_6H_4C{=}O}$$

The oxime of this ketone, when rearranged in the Beckmann manner, produced *m*-chlorophenylaceto-*p*-methoxyanilide. Assuming that a *cis* shift takes place between the groups, the oximes have the *anti* benzyl configuration.

The benzoin was reduced with tin and hydrochloric acid in alcoholic solution and both of the above ketones were found to be present in the reduction mixture. By careful fractional crystallization *p*-methoxybenzyl *m*-chlorophenyl ketone was obtained pure in about 10% yield. The major portion of the product, however, melted at 58–60° and proved to be a mixture of the two isomers as was shown by the fact that the melting point was raised when either ketone was added. A portion of the mixture was oximated and *m*-chlorobenzyl *p*-methoxyphenyl ketoxime was obtained by fractional crystallization in a yield of about 20%.

The evidence presented is thus conclusive proof that both isomeric desoxybenzoins are obtained in the reduction of this benzoin under the conditions of the experiment and is a further substantiation of the explanation of the mechanism of these reactions which was previously advanced.

Two other members of the series were prepared. Thus by condensing anisaldehyde with *m*-chlorobenzylmagnesium bromide *m*-chlorobenzyl-*p*-methoxyphenylcarbinol was obtained in a satisfactory yield. This carbinol

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(3) Jenkins, This Journal, 55, 703 (1933).

(4) Jenkins, *ibid.*, 55, 2896 (1933).

(5) Jenkins and Richardson, *ibid.*, 55, 1618 (1933).

could be easily dehydrated to form the corresponding stilbene, *sym-m*-chloro-*p'*-methoxydiphenylethylene.

It is our opinion that most, if not all, of the unsymmetrical benzoins, if reduced in the manner described here and in the preceding article, would be found to produce the two theoretically possible desoxy ketones. Although it is possible that reaction II might be very slow in comparison to I or that the glycol might even lose water to produce I, in every case so far studied both isomeric ketones have been obtained.

Experimental

Preparation of *m*-Chlorobenzanisoin

First Method.—To a solution of 13.60 g. of anisaldehyde, 14.00 g. of *m*-chlorobenzaldehyde and 70 cc. of alcohol was added 6.00 g. of potassium cyanide dissolved in 30 cc. of water. The mixture was refluxed on the water-bath for ninety minutes and placed in the refrigerator. After standing for twenty-four hours the crystalline material was separated, washed with water and recrystallized from slightly diluted alcohol. Yields of 25 to 30% were obtained. Recrystallized from a mixture of benzene and ligroin the substance was obtained as clusters of thick white prisms melting at 85.5° (corr.).

Second Method.—The Grignard reagent from 18.70 g. of *p*-bromoanisole and 2.50 g. of magnesium was prepared in the usual manner. After adding 4.64 g. of *m*-chloromandelamide[3] the solution was refluxed for twenty-five hours and then poured into 200 cc. of ice-cold 10% sulfuric acid. The mixture was stirred occasionally and allowed to stand at room temperature for two hours and then twice extracted with ether. The ether extract was steam distilled and the product was isolated as a yellow gum. After several crystallizations from dilute alcohol and then from benzene–ligroin the substance was obtained in a yield of about 20%, based on the amide used, as thick white prisms which proved to be identical with the compound prepared by method one.

***m*-Chlorobenzanisil.**—To a boiling alcoholic solution of the benzoin (water-bath) strong Fehling's solution was slowly added until an excess was present. After thirty minutes the hot solution was filtered and diluted with water. On standing the benzil separated and was recrystallized from dilute alcohol. The substance was obtained in a yield of about 50% as fine yellow needles which melted at 88° (corr.).

***sym-m*-Chloro-*p'*-methoxydiphenylethyleneglycol.**—This compound was obtained in a yield of about 60% by reducing the benzoin in alcoholic solution with 4% sodium amalgam at room temperature according to the method of preparing glycols which was described in article I.[1] The substance is soluble in alcohol and is best purified by recrystallization from a mixture of benzene and ligroin, from which it is obtained as white prisms melting at 101.5–102.5° (corr.).

Preparation of *p*-Methoxybenzyl *m*-Chlorophenyl Ketone

First Method.—Two grams of the glycol was dissolved in 20 cc. of glacial acetic acid containing 2.0 g. of concentrated sulfuric acid. The solution was refluxed for one hour in an apparatus with ground glass connections and then diluted with about 100 cc. of water. After standing for several hours the yellow solid was separated and recrystallized from dilute alcohol until pure. It consisted of colorless plates melting at 73–74° (corr.) and was obtained in a yield of about 25%. The mother liquors were carefully examined for the isomeric ketone but only gum-like material could be isolated.

Second Method.—A mixture of 5.00 g. of *m*-chlorobenzanisoin, 6.00 g. of mossy tin, 0.30 g. of copper sulfate, 30 cc. of concentrated hydrochloric and 50 cc. of alcohol was refluxed for seven hours and diluted with about 100 cc. of water. After standing for several hours the solid was separated. It weighed about 3.0 g. and melted at 55–65°. After several crystallizations from alcohol a fraction of about 0.60 g. consisting of colorless plates and melting at 73–74° was isolated. This substance proved to be identical with the ketone obtained in the dehydration of the glycol. The filtrates were combined and evaporated to about a third of the original volume and allowed to stand (continued below).

Third Method.—The Grignard reagent from 7.20 g. of *m*-chloroiodobenzene and 0.85 g. of magnesium was prepared in the usual manner. One and two-tenths grams of *p*-methoxyphenylacetamide was then added and the solution refluxed in an atmosphere of hydrogen for twenty-four hours. The ketone was obtained by means of the technique which has been described previously.[5] The yield in this case was not very good—about 20% based on the amide employed. The product proved to be identical in every respect with the substance obtained in methods one and two.

Almost quantitative yields of *p*-methoxyphenylacetamide are obtained by allowing a mixture of the methyl ester and concd. ammonium hydroxide to stand at room temperature for forty-eight hours. Practical purity is obtained by washing with ether; thin plates, m. p. 189–190° (corr.).

Preparation of *p*-Methoxybenzyl *m*-Chlorophenyl Ketoxime.—A mixture of 0.50 g. of the ketone prepared by either method, 0.50 g. of hydroxylamine hydrochloride, 0.80 g. of potassium acetate and 15 cc. alcohol was heated on the water-bath for three hours and diluted with enough hot water to dissolve the potassium chloride formed and cause a cloudiness. After standing in the refrigerator for several hours the solution deposited 0.45 g. of solid which after recrystallization from dilute alcohol consisted of white needles melting at 74–75° (corr.).

Rearrangement of *p*-Methoxybenzyl *m*-Chlorophenyl Ketoxime.—The oxime was rearranged with phosphorus pentachloride in absolute ether employing the technique described in a previous article.[5] The anilide thus obtained was compared (melting point and mixed melting point) with the two theoretically possible anilides, *viz.*, *p*-methoxyphenylacet-*m*-chloroanilide obtained by heating *p*-methoxyphenylacetic acid[6] with *m*-chloroaniline in an oil-bath at 180–190° for three hours and *m*-chlorobenzoyl-*p*-methoxybenzylamine, which was prepared in an analogous manner from *m*-chlorobenzoic acid and anisylamine.[7] The rearranged substance proved to be identical with the first anilide. This evidence thus establishes the structure of the ketone and indicates that the oxime has the *anti* benzyl configuration.

Preparation of *m*-Chlorobenzyl *p*-Methoxyphenol Ketone

First Method.—This ketone was prepared according to the Grignard method of obtaining desoxybenzoins recently described[5] by condensing *m*-chlorobenzylmagnesium bromide with *p*-methoxybenzamide. Four equivalents of the Grignard reagent to one equivalent of the amide were used and the mixture was heated for forty-eight hours. The ketone was obtained in a yield of 60% based on the amide employed. Recrystallized from alcohol it consists of white plates and melts at 70–71° (corr.).

Second Method.—The filtrate obtained in the second method of preparing *p*-methoxybenzyl *m*-chlorophenyl ketone (see above) on standing deposited about 2.0 g. of solid which after recrystallization from alcohol melted at 58–60° and proved to be a mixture of both ketones since when mixed with either the melting point was raised. Although the pure ketone could not be separated from this mixture after oximation the pure oxime was obtained (see below).

Preparation of *m*-Chlorobenzyl *p*-Methoxyphenyl Ketoxime.—This oxime was obtained from the Grignard ketone according to the general method[5] mentioned above in a

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(6) Mauthner, *Ann.*, **370**, 374 (1909).

(7) Goldschmidt and Polonowska, *Ber.*, **20**, 2407 (1887).

yield of 90% after crystallization from alcohol as white needles melting at 106.5–107.5° (corr.).

One gram of the mixture of ketones obtained in the reduction of the benzoin (see above) was oximated in a similar manner and after careful fractionation 0.22 g. of the pure oxime was obtained.

Rearrangement of *m*-Chlorobenzyl *p*-Methoxyphenyl Ketoxime.—The oxime was rearranged according to the method previously described[3] and the structure of the resulting anilide was established by comparison with the two theoretically possible anilides, *viz.*, *m*-chlorophenylacet-*p*-methoxyanilide obtained by heating *m*-chlorophenylacetic acid[4] and *p*-anisidine in an oil-bath for three hours at 170–190° and *p*-methoxybenzoyl-*m*-chlorobenzylamine prepared similarly from anisic acid and *m*-chlorobenzylamine.[5] The anilide obtained by rearrangement proved to be identical with the first synthetic product. The oxime thus has the *anti* benzyl configuration.

Preparation of *m*-Chlorobenzyl-*p*-methoxyphenylcarbinol.—The Grignard reagent of 0.10 mole of *m*-chlorobenzyl bromide and 2.50 g. of magnesium was prepared in the usual manner. To the solution 12.0 g. of anisaldehyde dissolved in 100 cc. of absolute ether was added. The mixture was heated and mechanically stirred for two hours and then poured into 200 cc. of ice-cold 10% ammonium chloride solution. After extraction with ether, drying with anhydrous sodium sulfate and evaporating the solvent *in vacuo* the carbinol was obtained as a yellow viscous oil in a yield of about 75%. Considerable

TABLE I

CONSTANTS AND ANALYTICAL DATA OF *m*-CHLOROBENZANISOIN AND DERIVATIVES

Compound	Appearance	M. p., °C. (corr.)	Mol. wt. (Rast) Calcd.	Mol. wt. (Rast) Found	Formula	Chlorine, % (Parr bomb) Calcd.	Chlorine, % (Parr bomb) Found
Benzil	Fine yellow needles	88	274.5	263	$C_{15}H_{11}ClO_3$	12.91	13.01
Benzoin	Cream granules	85.5	276.5	287	$C_{15}H_{13}ClO_3$	12.81	12.96
Hydrobenzoin	White prisms	101.5–102.5	278.5	277	$C_{15}H_{15}ClO_3$	12.72	12.87
p-Methoxybenzyl-*m*-chlorophenyl ketone	White plates	73–74	260.5	241	$C_{15}H_{13}ClO_2$	13.60	13.68
m-Chlorobenzyl-*p*-methoxyphenyl ketone	White plates	70–71	260.5	263	$C_{15}H_{13}ClO_2$	13.60	13.92
m-Chlorobenzyl-*p*-methoxyphenyl carbinol	Thick white plates	42–43	262.5	285	$C_{15}H_{15}ClO_2$	13.50	13.30
Stilbene	Cream leaves	96	244.5	228	$C_{15}H_{13}ClO$	14.50	14.68

TABLE II

CONSTANTS AND ANALYTICAL DATA OF OXIMES AND ANILIDES

Phenyl ketoxime	Appearance	M. p., °C. (corr.)	Chlorine found, %
Anti-*p*-methoxybenzyl-*m*-chloro-	White needles	74–75	13.00
Anti-*m*-chlorobenzyl-*p*-methoxy-	White needles	106.5–107.5	13.09

Amide	Appearance	M. p., °C. (corr.)	Chlorine found, %
m-Chlorophenylacet-*p*-methoxyanilide	Long, thin plates	148.5	12.93
p-Methoxybenzoyl-*m*-chlorobenzylamine	Soft, white plates	161	12.89
p-Methoxyphenylacet-*m*-chloroanilide	Thin plates	86.5	12.85
m-Chlorobenzoyl-*p*-methoxybenzylamine	Colorless leaves	92.5	12.60

The oximes and amides all have the molecular formula $C_{15}H_{14}NClO_2$ and calculated chlorine content of 12.90%.

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(5) This amine was obtained by reducing *m*-chlorobenzaldoxime with zinc and acetic acid according to the method of Frantzen [*Ber.*, **38**, 1415 (1905)] for preparing the *o*-chloro isomer. The procedure was shortened, however, by steam distilling the crude amine rather than separating it as the carbonate; colorless oil, b. p. 105–110° (13 mm.). See also Braun, Kühn and Weismantel [*Ann.*, **449**, 273 (1926)] for a catalytic method of preparation.

difficulty was experienced in inducing the substance to crystallize. Success was attained, however, by dissolving it in a warm mixture of benzene and ligroin and seeding with a few crystals which were obtained by allowing a little of the solution to remain on a watch glass at room temperature for several days. The substance was obtained as thick, white plates melting at 43–44° (corr.).

Preparation of *sym-m*-Chloro-*p'*-methoxydiphenylethylene.—This stilbene was obtained in 60% yield by heating for thirty minutes the above carbinol with twenty parts of a solution consisting of 20% concentrated hydrochloric acid in glacial acetic acid. The crude material was isolated by diluting the solution with water. Recrystallized from alcohol the substance was obtained as cream colored leaves melting at 96° (corr.).

Summary

The explanation of the mechanism of the reduction of unsymmetrical benzoins which was previously advanced has been substantiated in the present work.

m-Chlorobenzanisoin, which has not been described previously, is shown to be *m*-chloro-*α*-hydroxybenzyl *p*-methoxyphenyl ketone by an independent synthesis.

When reduced under suitable conditions this benzoin was found to produce *m*-chlorobenzyl *p*-methoxyphenyl and *p*-methoxybenzyl *m*-chlorophenyl ketones, the structures of which were established. In the course of this work thirteen new compounds were prepared and characterized.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Some Mono and Dibromo Derivatives of Meta Cresol. II

BY RALPH C. HUSTON AND WALTER J. PETERSON

In a recent report[1] from this Laboratory several new bromo derivatives of *m*-cresol were prepared and their structures conclusively proved. A continuation of this work has resulted in the preparation of several new derivatives. Two new methods for the protection of positions during bromination have been developed.

6-Bromo-*m*-cresols

From 6-Amino-*m*-cresols.—Pure *m*-cresol was nitrated according to the method of Staedel and Kolb,[2] and the isomeric products separated by steam. The volatile 6-nitro product (m. p. 56°) was converted to the 6-amino hydrochloride by reduction in alcohol with stannous chloride and hydrochloric acid.[3] Attempts to change the hydrochloride (m. p. 212°) to the free base were unsuccessful. The free amine (m. p. 157°) may be obtained by reduction of the nitro compound in accordance with the method of Hodgson and Beard.[4] 6-Nitro-*m*-cresol (33 g.) was treated with 400 cc. of water containing

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(1) Huston and Hutchinson, THIS JOURNAL, **54**, 1504 (1932).

(2) Staedel and Kolb, *Ann. Chem.*, **259**, 210 (1890).

(3) (a) Raiford and Leavell, THIS JOURNAL, **36**, 1505 (1914); (b) Raiford, *Am. Chem. J.*, **46**, 419 (1911).

(4) Hodgson and Beard, *J. Chem. Soc.*, **127**, 498 (1925).

60 g. of sodium carbonate. This was treated at the boiling point with 126 g. of solid sodium hydrosulfite. 6-Amino-*m*-cresol[5] was deposited on cooling in almost colorless fine needles melting at 157–159°.

Ten grams of the hydrochloride, dissolved in 16 g. of concd. sulfuric acid and 80 cc. of water, was diazotized below 20° with a solution of 6 g. of sodium nitrite in 125 cc. of water. Replacement of the diazonium group with bromine was effected by dropping the solution into a hydrobromic acid–cuprous bromide solution[6] (from 5 g. of copper sulfate), while a vigorous current of steam was passed through the reaction mixture. The oil in the distillate was extracted with ether and distilled. Four grams of 6-bromo-*m*-cresol came over at 81–82° (4 mm.). The identity with the product formed by direct bromination[1] was proved by boiling point at atmospheric pressure, analysis and bromination[7] to 4,6-dibromo-*m*-cresol[1] (m. p. 65–66°), the benzoyl ester of which melted at 84–85°.

2-Bromo-*m*-cresol

From 2-Nitro-*m*-cresol.—Nitration of *m*-cresol was carried out in fuming sulfuric acid of higher sulfur trioxide content than that used by Gibson,[8] or Hodgson and Beard.[4] A cold solution of 150 g. of *m*-cresol in 100 cc. of fuming sulfuric acid (23% SO_3) was treated with a mixture of 100 cc. of fuming sulfuric acid and 46 cc. nitric acid (1.5) and allowed to stand overnight. The mixture was diluted with 500 cc. of water and heated to 180° on an oil-bath. Decomposition with superheated steam gave 43 g. of 2-nitro-*m*-cresol (m. p. 39°) and 40 g. of *m*-cresol.

Reduction of 33 g. of the nitrocresol by means of sodium hydrosulfite gave 20 g. of 2-amino-*m*-cresol. Eleven grams of this gave, upon diazotization and decomposition with hot hydrobromic acid–cuprous chloride solution (see above), 7.5 g. of an oil which boiled at 83–84° (4 mm.) and solidified on standing. Recrystallization from alcohol gave large monoclinic crystals melting at 58.5–59°.

Anal. Calcd. for C_7H_7OBr: Br, 42.78. Found: Br, 42.62.

A portion of the 2-bromo-*m*-cresol, brominated in cold carbon tetrachloride with one mole of bromine, yielded a portion of uncrystallizable oil (probably 2,6-dibromo-*m*-cresol) and a crystalline fraction which was proved to be 2,4-dibromo-*m*-cresol by melting point (65°) and ester formation.

Methylation of the sodium salt of 2-bromo-*m*-cresol by means of methyl iodide gave a methyl ether melting at 39.5–40°. Hodgson and Beard[4] give 35.5–36.5°.

Anal. Calcd. for C_8H_9OBr: Br, 41.13. Found: Br, 40.98.

By Bromination in Fuming Sulfuric Acid.—To a cold solution of 108 g. of *m*-cresol in 450 cc. of fuming sulfuric acid (23% SO_3), 160 g. of bromine was added very slowly. After 24 hours, the liquid was diluted with 500 cc. of water and heated on an oil-bath to 180°. Steam was passed through the hot solution for about three hours, during which time the temperature was maintained between 180 and 210°. Repeated distillations of the product, using a 20-cm. column and a vacuum of 4 mm., resulted in a large fraction (100.7 g.) boiling at 80–85° and 13.5 g. boiling at 114–116°. The 80–85° fraction, when seeded with a crystal of the 2-bromo-*m*-cresol prepared by diazotization, crystallized immediately. After standing overnight in an ice box, the 2-bromo-*m*-cresol, which made up more than half of the weight of the fraction, was filtered off by suction and recrystallized from alcohol, m. p. 58.5–59°. The uncrystallizable oil came over after refractionation at 80–81° (4 mm.). Preparation of its benzene sulfonyl ester

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(5) Auwers, Borsche and Weller, *Ber.*, **54**, 1315 (1921).

(6) Bigelow, "Organic Syntheses," Vol. V, p. 21.

(7) Bromination in cold chloroform with 1 mole of bromine gave, in addition to 4,6-dibromo-*m*-cresol, a small amount of oil having the properties of 2,6-dibromo-*m*-cresol.

(8) Claus, *J. prakt. Chem.*, [2] **39**, 61 (1888).

(m. p. 92–93°) proved it to be 6-bromo-*m*-cresol. Ester formation of the fraction boiling at 114–116° proved it to be 2,6-dibromo-*m*-cresol.

By Bromination of the Disulfonic Acid in Alkaline Solutions.—A mixture of one mole (108 g.) of *m*-cresol and 3.5 moles (350 g.) of concentrated sulfuric acid in a three-liter three-necked flask was heated on a steam-bath for three to four hours. At the end of this time the reaction mixture was cooled, the stirring motor attached and the mixture made alkaline with a solution of 7 moles (280 g.) of sodium hydroxide dissolved in 700 cc. of water. The alkaline solution was then cooled to room temperature and brominated slowly with one mole (160 g.) of bromine (during this operation the temperature may be allowed to rise to 40–50°). The mixture was then steam distilled over an oil-bath at 150°. This removed any tribromo-*m*-cresol present. When no more of the tribromo product was observed in the distillate, the distillation was stopped and the mixture, still on the oil-bath, evaporated to a thick pasty mass. This was then allowed to cool and acidified with 800 cc. of concentrated sulfuric acid. (This must be done slowly due to the rapid evolution of hydrogen bromide.) The mixture was again distilled by steam, this time in an oil-bath at 200–210°. The distillate on fractionation gave 37.3 g. boiling at 80–85° (4 mm.) which crystallized on being seeded with 2-bromo-*m*-cresol. From this fraction 13.1 g. of an uncrystallizable oil was separated which boiled at 80–81° (4 mm.) and which was identified as 2-bromo-*m*-cresol. This method of bromination yields a larger portion (43.0 g.) of the 2,6-dibromo-*m*-cresol boiling at 114–116° (4 mm.) than does bromination in fuming sulfuric acid.

2,6-Dibromo-*m*-cresol

From *p*-Nitro-*m*-cresol.—Fifty-eight grams of *p*-nitro-*m*-cresol, when brominated in glacial acetic acid at 15–20° with two moles of bromine, yielded 56.9 g. of 2,6-dibromo-4-nitro-*m*-cresol[8] melting at 134°.

The hydrochloride of 2,6-dibromo-4-amino-*m*-cresol was prepared by reduction in alcohol with stannous chloride and hydrochloric acid according to the method of Raiford.[3b]

For replacement of the amino group with bromine, a modification of the procedure of Bigelow, Johnson and Sandborn[9] for the preparation of *m*-bromotoluene was used. To a cold mixture of 48 cc. of 45% alcohol and 12 cc. of sulfuric acid in one-liter round-bottomed flask provided with a mechanical stirrer was added 20 g. of the hydrochloride of 2,6-dibromo-4-amino-*m*-cresol. The solution was cooled to 10° and a solution of 9 g. of sodium nitrite in 16 cc. of water was added from a separatory funnel. Stirring was continued for a half hour. To the diazotized solution was added 3 g. of reduced copper powder. The stirrer was replaced by a reflux condenser. The flask was warmed cautiously until a vigorous evolution of gas began and was then immersed in ice water. When the reaction had moderated, the flask was heated for ten minutes on a steam-bath. One hundred and twenty cc. of water was added and the mixture was steam distilled. The distillate, after washing and extraction, was fractionated. The bulk of the yellow oil (8.3 g.) came over at 114–116° (4 mm.).

Anal. Calcd. for $C_7H_6OBr_2$: Br, 60.15. Found: Br, 60.32.

A portion of the oil brominated in carbon tetrachloride in the cold yielded 2,4,6-tribromo-*m*-cresol, melting at 80–81°.[10]

By Bromination of the Para Sulfonic Acid in Alkaline Solution.—A mixture of one mole (108 g.) of *m*-cresol and one mole of concentrated sulfuric acid (96 g.) in a two-liter three-necked flask was heated in a water-bath for three hours. The mixture was then cooled and 160 g. of sodium hydroxide in 375 cc. of water was added. The alka-

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(9) Bigelow, Johnson, Sandborn, "Organic Syntheses," Vol. VI, p. 16.

(10) Werner, *Bull. soc. chim.*, 2, 46, 276; Auwers and Richter, *Ber.*, **32**, 3382 (1899); Bures and Balada, *Casopis Ceskoslov. Lekamista*, [6] **107**, 190 (1926).

line solution was cooled to room temperature and brominated (40–50°) with 320 g. of bromine. The rest of the procedure (steam distillation, evaporation and distillation) was carried out as in the preparation of 2-bromo-*m*-cresol by the similar method. The fractionated distillate yielded, besides some tribromo-*m*-cresol, 48 g. of 2,6-dibromo-*m*-cresol. Esters were prepared by the method of Einhorn and Holland.[11]

TABLE I

Benzoyl ester of *m*-cresol	Crystals from alcohol	M. p., °C.	Bromine, % Calcd.	Bromine, % Found
2-Bromo	Small colorless plates	59 – 60	27.49	27.58
6-Bromo	Small needles	87.5– 88	27.49	27.58
2,4-Dibromo	Fine needles	81 – 81.5	43.24	43.18
2,6-Dibromo	Fine needles	89.5– 90	43.24	43.40
2,4,6-Tribromo	Small needles	84 – 85	53.45	53.39
Benzene sulfonyl ester of *m*-cresol				
2-Bromo	Small plates	70 – 71	24.46	24.39
6-Bromo	Small plates	92 – 93	24.46	24.34
2,4-Dibromo	Small plates	92 – 92.5	39.41	39.49
2,6-Dibromo	Small plates	94 – 95	39.41	39.52
2,4,6-Tribromo	Plates	117 –117.5	49.28	49.20
p-Toluene sulfonyl ester of *m*-cresol				
2-Bromo	Needle-like plates	85 – 85.5	23.43	23.34
6-Bromo	Needle-like plates	72.5– 73	23.43	23.52
2,4-Dibromo	Small plates	89.5– 90	38.00	38.13
2,6-Dibromo	Fine needles	122 –123	38.00	38.09
2,4,6-Tribromo	Small plates	113 –114	48.09	48.17

Summary

1. New bromine derivatives of *m*-cresol were prepared.

2. A new method for the bromination of *m*-cresol in fuming sulfuric acid was developed.

3. Simple diazotization methods have been found applicable for the replacement of amino groups in phenolic compounds with hydrogen and bromine.

EAST LANSING, MICHIGAN

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[11] Einhorn and Holland, *Ann.*, **301**, 95 (1898).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Triphenylvinyl Mercaptan

BY C. F. KOELSCH AND GLENN ULLYOT

Thiophenols may be obtained, often in good yields, by the action of sulfur on arylmagnesium halides.[1] Triphenylvinylmagnesium bromide reacts with sulfur in an analogous manner, giving the corresponding thiol, $(C_6H_5)C{=}C(SH)C_6H_5$.

A few thiols have been described in which the sulfhydryl group is attached to an unsaturated aliphatic carbon atom,[2] but the carbonyl group which each of these compounds contains probably influences the behavior of the sulfhydryl group. On alkylation, these substances give S-ethers,[3] and on treatment with phenylhydrazine or with hydroxylamine they evolve hydrogen sulfide with the formation of phenylhydrazones or oximes, indicating that they react in the tautomeric forms $C{=}C{-}SH$ and $CH{-}C{=}S$.

In contrast, triphenylvinyl mercaptan appears to react in only the enol form. It dissolves readily in aqueous sodium hydroxide, slowly in boiling aqueous sodium carbonate; carbon dioxide precipitates the mercaptan from these solutions. Methyl sulfate and alkali give a S-methyl ether, and benzoylation by the Schotten–Baumann reaction gives a benzoate. Boiling with alcoholic hydroxylamine acetate gives bis-triphenylvinyl disulfide, which may also be obtained by oxidizing the mercaptan with permanganate. Acid hydrolysis of the mercaptan yields diphenylacetophenone.

Diphenylacetophenone, the O-analog of triphenylvinyl mercaptan, was for a long time considered as triphenylvinyl alcohol, since it could be acetylated and since it supposedly did not form an oxime.[4] At the present time, however, it is given the ketonic formula, Kohler having shown that under the proper conditions it forms an oxime and adds alkylmagnesium halides.[5] Furthermore, diphenylacetophenone is insoluble in alkalies, while the closely related 9-benzoylfluorene is known in a keto and an enol form, the latter of which is readily soluble in aqueous alcoholic alkali, while the former is slowly soluble, solution being accompanied by enolization.[6] The present results indicate that sulfur has little tendency to form a double bond with carbon, a conclusion which may also be drawn from the readiness with which aliphatic thioaldehydes and ketones polymerize, and from the reactivity and color of the aromatic thioketones.

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(1) Taboury, *Bull. soc. chim.*, [3] **33**, 836 (1905).

(2) $C_6H_5CH{=}C(SH)COOH$, Granacher, *Helv. Chim. Acta.*, **5**, 610 (1922); $CH_3C(SH){=}CH{-}COOC_2H_5$, Scheibler and Bube, *Ber.*, **48**, 1451 (1915).

(3) Mitra, *J. Indian Chem. Soc.*, **10**, 71 (1933).

(4) Biltz, *Ber.*, **32**, 650 (1899).

(5) Kohler, *Am. Chem. J.*, **36**, 191 (1906).

(6) Meyer and Gottlieb-Billroth, *Ber.*, **54**, 575 (1921); *cf.* Ley and Manecke, *ibid.*, **56**, 777 (1923).

Experimental

Triphenylvinyl Mercaptan.—To a solution of triphenylvinylmagnesium bromide containing two grams of magnesium[7] is added 2.2 g. of sulfur, and the mixture is refluxed for two hours. The magnesium compound is hydrolyzed with iced sulfuric acid, the ether is removed, and the sirupy residue is crystallized from benzene and then from ligroin; yield, 12 g. The compound forms faintly yellow needles that melt at 110–111°.

Anal. Calcd. for $C_{20}H_{16}S$: C, 83.3; H, 5.6. Found: C, 83.5; H, 5.5. *Mol. wt.* Calcd.: 288. Found: (Rast) 275.

Triphenylvinyl mercaptan dissolves in warm aqueous sodium hydroxide, giving a yellow solution which deposits the white difficultly soluble salt on cooling. On boiling with sodium carbonate solution, the mercaptan slowly dissolves; carbon dioxide passed into a warm solution of the sodium salt precipitates the mercaptan.

When a solution of 1 g. of the mercaptan in 30 ml. of acetic acid is acidified with a few drops of sulfuric acid and then boiled, hydrogen sulfide is evolved. On cooling this solution, diphenylacetophenone crystallizes in a nearly theoretical yield. The product melts at 134.5–135° alone or mixed with an authentic sample, and gives the characteristic green color on heating with concd. sulfuric acid.

The methyl ether is obtained by shaking a solution of 1 g. of the mercaptan and 2 g. of sodium hydroxide in 40 ml. of water with 3 ml. of methyl sulfate for twelve hours. The product, crystallized from methanol, forms orange-yellow prisms (0.8 g.) that melt at 109.5–110°. The methyl ether is insoluble in hot sodium hydroxide solution, but very easily soluble in the common organic solvents including petroleum ether; a mixture with triphenylvinyl mercaptan melts at 86–89°. On boiling the methyl ether with acetic acid containing a little sulfuric acid, methyl mercaptan is evolved.

Anal. Calcd. for $C_{21}H_{18}S$: C, 83.4; H, 6.0. Found: C, 83.3; H, 6.0.

The benzoate, prepared by the Schotten–Baumann reaction and crystallized from acetic acid, forms colorless needles that melt at 192–193°. Concordant analytical results were difficult to obtain.

Anal. Calcd. for $C_{27}H_{20}OS$: C, 82.5; H, 5.1. Found: C, 81.6; H, 5.2.

Bis-triphenylvinyl Disulfide.—To a solution of 1 g. of triphenylvinyl mercaptan in hot sodium hydroxide is added 1 g. of potassium permanganate. The mixture is made faintly acid and filtered. The solid is dried and extracted repeatedly with hot ligroin (b. p. 90–110°). The disulfide is obtained by concentrating and cooling the combined extracts. On recrystallization from acetic acid there is obtained about 0.4 g. of yellow prisms that melt at 179.5–180.5° and give a qualitative test for sulfur.

Anal. Calcd. for $C_{40}H_{30}S_2$: C, 83.6; H, 5.3. Found: C, 83.8; H, 5.7. *Mol. wt.* (Rast). Calcd. 574. Found: 585.

The disulfide is obtained when a solution of the mercaptan in alcohol is boiled for four hours with an excess of hydroxylamine hydrochloride and sodium acetate.

Summary

Triphenylvinyl mercaptan, obtained from triphenylvinylmagnesium bromide and sulfur, behaves as an enolic substance, in contrast to its O-analog, diphenylacetophenone.

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[7] Koelsch, THIS JOURNAL, 54, 2047 (1932).

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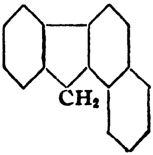
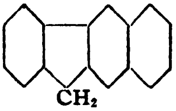
A Synthesis of 2,3-Benzofluorene

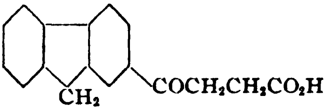
BY C. FREDERICK KOELSCH

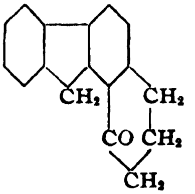
Since degradation experiments with the hydrocarbon obtained by the action of sodium on 1-diphenylene-3-phenylindene[1] have given results of no value as a structure proof, the problem is being attacked by synthesis. One possible synthesis requires 1,2-benzofluorene (I) as an intermediate. The present paper describes a synthesis which might have led to this hydrocarbon, but which gives its isomer, 2,3-benzofluorene (II), instead.

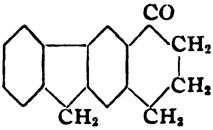

I


II

Fluorene and succinic anhydride condense to β-2-fluoroylpropionic acid (III), the orientation of which is shown by oxidation. Reduction of this keto acid gives γ-fluorylbutyric acid. Now although cyclization of this acid by treating its chloride with aluminum chloride may lead to (IV) or (V), actually only one substance is formed.


III


IV


V

The structure of this product is not clearly predictable, since strictly analogous cases have not been investigated previously. γ-2-Naphthylbutyric acid undergoes only angular condensation to form (VI),[2,3] but such a result is occasioned by the known greater reactivity of the α as compared with the β position in the naphthalene nucleus. The more closely related γ-2-tetralylbutyric acid behaves peculiarly, in that it is cyclized by sulfuric acid exclusively to the linear product (VII),[4] while thermal decomposition of its chloride gives a mixture of about equal parts of the linear (VII) and the angular (VIII) products.[5]

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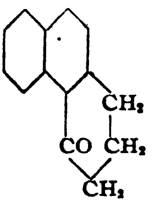
(1) Koelsch, THIS JOURNAL, 55, 3398 (1933).

(2) Schroeter, Mueller and Huang, *Ber.*, 62, 645 (1929).

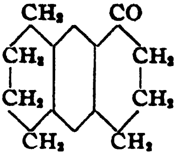
(3) Haworth, *J. Chem. Soc.*, 1126 (1932).

(4) Krollpfeiffer and Schäfer, *Ber.*, 56, 620 (1923).

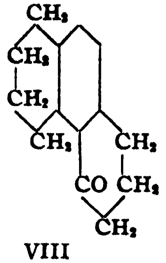
(5) Schroeter, *ibid.*, 57, 2003 (1924).



VI



VII



VIII

The nitration of 2-acetylaminofluorene, which gives the 3-nitro compound[6] and not the 1-nitro compound as was formerly believed,[7] is quite significant as an indication of the greater reactivity of the 3-position in the fluorene nucleus substituted in the 2-position by an *o,p*-directing group.

The further transformations of the cyclization product obtained in the present investigation show it to be the linear (2,3-) compound (V). On reduction it gives tetrahydrobenzofluorene, and this is dehydrogenated to the known 2,3-benzofluorene (II).

Experimental

β-2-Fluoroylpropionic Acid.—To a stirred suspension of 50 g. of succinic anhydride and 85 g. of fluorene in 500 ml. of benzene is added 150 g. of aluminum chloride in portions. The mixture is then heated for one hour on a water-bath with stirring. The reaction mixture is hydrolyzed in the usual way, and the benzene is steam distilled. The solid acid remaining is best purified through its sodium salt, which is easily soluble in hot water and difficultly soluble in cold water. The free acid, obtained in yields of 75–86% after crystallization from acetic acid, forms needles that melt at 210–212°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.6; H, 5.3. Found: C, 76.5; H, 5.3.

On boiling the keto acid (1 g.) for two hours in acetic acid with 2 g. of sodium dichromate, there is obtained *β-fluorenonoylpropionic acid* which crystallizes from acetic acid in yellow plates that melt at 230–234° with previous darkening.

Anal. Calcd. for $C_{17}H_{12}O_4$: C, 72.8; H, 4.3. Found: C, 72.6; H, 4.6.

Fluoroylpropionic acid dissolved in dilute soda solution is rapidly and completely oxidized on boiling with the calculated amount of potassium permanganate to fluorenone-2-carboxylic acid, yellow needles from acetic acid that do not melt at 295° (literature,[8] >275°). This acid, with thionyl chloride and methanol, gives the methyl ester, yellow needles from methanol that melt at 177–181° (literature,[9] 181°).

Methyl β-2-fluoroylpropionate obtained from the keto acid (5 g.), methanol (75 ml.), and concd. sulfuric acid (5 ml.) by refluxing for four hours, forms white plates from methanol that melt at 111–112°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.2; H, 5.7. Found: C, 77.2; H, 5.8.

The methyl ester oxime, recrystallized from benzene–ligroin, forms needles that melt at 129–130°.

Anal. Calcd. for $C_{18}H_{17}O_3N$: C, 73.2; H, 5.8. Found: C, 73.5; H, 5.8.

γ-Fluorylbutyric Acid.—The usual Clemmensen method does not affect the keto

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(6) Eckert and Langecker, *J. prakt. Chem.*, [2] 118, 263 (1928).

(7) Diels, *Ber.*, 35, 3285 (1902).

(8) Bamberger and Hooker, *Ann.*, 229, 158 (1885).

(9) Fortner, *Monatsh.*, 25, 451 (1904).

acid, but by carrying out the reduction in aqueous alcohol, nearly quantitative yields are obtained.

A mixture of 90 g. of fluoroylpropionic acid, 450 ml. of alcohol, 450 ml. of concd. hydrochloric acid and 180 g. of amalgamated zinc is boiled for one hour, an additional 450 ml. of concd. hydrochloric acid is added, and boiling is continued for eight hours. The mixture is cooled, the solid is separated and boiled with one liter of 5% sodium hydroxide until all of the organic matter is dissolved. The solution is filtered and acidified, giving 85 g. of a product that melts at 142–146°. Recrystallization of a portion from acetic acid and then from benzene–ligroin gives white plates that melt at 151–151.5°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found: C, 80.6; H, 6.5.

Ketotetrahydrobenzofluorene.—Distillation of γ-fluorylbutyric acid with phosphorus pentachloride,[3] or heating with 85% sulfuric acid[3] does not cause ring closure. The acid reacts with thionyl chloride to give a black tar which does not have the properties of an acid chloride.

Ring closure is satisfactorily effected as follows: 25 g. of fluorylbutyric acid is refluxed in benzene (250 ml.) with 21 g. of phosphorus pentachloride until the evolution of hydrogen chloride ceases. The solution is cooled and 20 g. of aluminum chloride is added with stirring. After refluxing for thirty minutes, the mixture is poured onto ice and hydrochloric acid, and the benzene is steam distilled. The solid product is dissolved in acetic acid (300 ml.) and boiled with charcoal. The addition of water precipitates 18 g. of light tan colored plates, m. p. 135–140°. Distillation at 20 mm. followed by crystallization from acetic acid is carried out with practically no loss; the ketone forms white plates that melt at 148–149°. It may be distilled without decomposition at atmospheric pressure.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 86.9; H, 6.1.

The semicarbazone, crystallized from acetic acid, forms needles which become brown at 250°, but do not melt at 290°.

Anal. Calcd. for $C_{18}H_{17}ON_3 + CH_3COOH$: C, 68.3; H, 6.0. Found: C, 68.0; H, 6.1.

Tetrahydrobenzofluorene.—Ketotetrahydrobenzofluorene is reduced readily by the usual Clemmensen procedure, four hours boiling sufficing for complete reduction. The crude solid obtained, which is contaminated with a little dimolecular reduction product, is distilled under reduced pressure and crystallized from acetic acid; yield, 60–70%. The hydrocarbon forms white plates that melt at 129°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.8; H, 7.6.

The picrate forms orange-red needles from absolute alcohol that melt at 123–124°.

2,3-Benzofluorene.—Tetrahydrobenzofluorene (3.2 g.) is heated at 250–275° with sulfur (1.6 g.) until the evolution of hydrogen sulfide ceases (about one hour). The violet melt, from which no crystalline substance can be obtained directly, is distilled under reduced pressure. The deeply colored distillate is crystallized from toluene, giving 0.4 g. of benzofluorene that melts at 204–206° (literature,[10] 208°). On oxidation with sodium dichromate in acetic acid, this hydrocarbon gives 2,3-benzofluorenone, yellow needles that melt at 146–148° (literature,[10] 152°).

The analyses reported in this paper were carried out by Mr. P. O. Tawney.

Summary

A synthesis of 2,3-benzofluorene starting with fluorene has been described.

MINNEAPOLIS, MINNESOTA

RECEIVED JUNE 24, 1933
PUBLISHED SEPTEMBER 5, 1933

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[10] Thiele and Wanscheidt, *Ann.*, 376, 276 (1910).

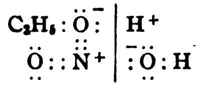
Notes

Explanation of the Formation of Alkyl Nitrites in Dilute Solutions; Butyl and Amyl Nitrites

BY WILLIAM A. NOYES

That nitrous acid is amphoteric, giving both hydrogen and hydroxyl ions in the same manner as hypochlorous acid,[1] is shown by the blue color of nitrous anhydride developed when a dilute acid is added to an ice cold solution of sodium nitrite. Ethyl alcohol is an acid, giving hydrogen ions, as is shown by the action of metallic sodium, by the conductivity of absolute alcohol, which is less than that of pure water, and by the probability of a trifling volatilization of calcium ethylate, $Ca(OC_2H_5)_2$, when absolute alcohol is distilled over calcium oxide.[2] That it is not amphoteric, giving hydroxyl ions, to any appreciable extent is shown by the fact that ethyl ether has never been found in absolute alcohol.

Many years ago Wallach and Otto[3] described a method of preparing ethyl nitrite from dilute alcohol and nitrous acid but they made no remark on the surprising character of this reaction in comparison with those used for the preparation of esters of other weak acids. The explanation is apparent from the considerations given above. The alcohol reacts as an acid and the nitrous acid as a base:



$$\begin{array}{r|l} C_2H_5:\overset{\cdot\cdot}{O}\!:^{-} & H^+ \\ \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}::\overset{\cdot\cdot}{\overset{\cdot\cdot}{N}}{}^{+} & {}^{-}\!:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H \end{array}$$

The following method of preparing butyl and amyl nitrites, which is much simpler and quicker than those described in the literature,[4] has been developed by careful experiments on the basis of the principles given.

Dilute 14.5 cc. of concd. sulfuric acid of 96% (one-fourth mole) with 10 cc. of water, cool to 0°, add 39 g. (one-half mole = 37 g.) of normal butyl alcohol or 46 g. of amyl alcohol and cool again. Introduce the resulting homogeneous mixture, during five to ten minutes, beneath the surface of 38 g. of sodium nitrite dissolved in 150 cc. of water. The nitrite solution is cooled in a dish containing ice and water and the contents kept thoroughly mixed by a rapid, whirling motion. Remove the flask from the ice water and allow it to stand for a few minutes until the contents separates in three layers, butyl nitrite above, a saturated solution of sodium sulfate and crystals of sodium sulfate below. Separate sharply in a separatory funnel and wash twice by shaking vigorously with 10 cc. of a solution of 25 g. of salt and 2 g. of acid sodium carbonate in 100 cc. of water.

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(1) W. A. Noyes and T. A. Wilson, THIS JOURNAL, **44**, 1030 (1922). S. Goldschmidt, *Ber.*, **52**, 753 (1919), had previously shown the same fact by distilling a solution of hypochlorous acid at a very low temperature but he did not appreciate the theoretical importance of his experiment.

(2) Noyes, THIS JOURNAL, **45**, 861 (1923).

(3) Wallach and Otto, *Ann.*, **253**, 251 (1889). See also, Noyes, "Organic Chemistry for the Laboratory," fifth edition, p. 285.

(4) R. Adams and O. Kamm, THIS JOURNAL, **40**, 1285 (1918); last English translation of Gattermann-Wieland, p. 136.

If the nitrite is to be used for a purpose where a little water will do no harm, no further purification is required and the yield is 93 to 95% on the basis of the sulfuric acid used. After standing for a day or two with anhydrous sodium sulfate, the yield is about 90%. The nitrite retains a very small amount of the alcohol used. This is very rarely objectionable but it may be removed by careful distillation with a good column, under diminished pressure. Distillation under atmospheric pressure causes some decomposition.

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED MAY 26, 1933
PUBLISHED SEPTEMBER 5, 1933

Aliphatic Hydrocarbons in "Lorol"[1]

BY JOHN R. RUHOFF[2]

Since "Lorol" has recently become available in large quantities, it is one of the best sources of higher aliphatic alcohols. In the course of the distillation of fifty pounds of this material, certain small intermediate fractions were obtained whose presence could not be immediately accounted for. Investigation showed them to be azeotropic mixtures of a paraffin hydrocarbon and an alcohol in the ratio of about 1 to 2.

One of the fractions, boiling at 187–188° (wt. 185 g.), was shaken with benzoyl chloride and sodium hydroxide solution and distilled. Octyl benzoate and a liquid insoluble in concentrated sulfuric acid were recovered. A fraction, boiling at 157–158° (100 mm.) (wt. 105 g.), when treated in a similar manner, yielded decyl benzoate and again an oil insoluble in sulfuric acid. The properties of these two substances, as given in Table I, indicate definitely that they were *n*-undecane and *n*-tridecane.

It seems very probable that, during the high-pressure reduction of the coconut oil, these hydrocarbons were also formed, by the hydrogenolysis

TABLE I

PHYSICAL CONSTANTS OF HYDROCARBONS ISOLATED FROM "LOROL"

	From fraction boiling at 187–188°	*n*-Undecane	From fraction boiling at 157–158° at 100 mm.	*n*-Tridecane
M. p., °C.	−28[a]	−25.65[b]	−6	−6.2[c]
B. p., °C.	195–198	195.84[b]	161–165 (100 mm.)	162.5[c] (100 mm.)
d_4^{20}	0.7457	0.73667[b]	0.7543	0.7534[d]
$n_D^{25°}$	1.4200	1.41727[b]	1.4250	1.4250[e]

[a] The melting point was not depressed by the admixture of some authentic *n*-undecane. [b] Shepard, Henne and Midgley, THIS JOURNAL, 53, 1948 (1931). [c] Krafft, *Ber.*, 15, 1699 (1882). [d] Calculated from the data of Krafft. [e] Estimated from the data of Shepard, Henne and Midgley.

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(1) Trade name of a commercial product consisting of a mixture of aliphatic alcohols formed by the high-pressure hydrogenation of coconut oil.

(2) Kewaunee Manufacturing Company Fellow in Chemistry.

of an alcohol containing one more carbon atom, as described by Wojcik and Adkins.[3] No other hydrocarbon was isolated in quantity sufficient for identification, although there was some evidence that a fraction boiling at 130–50° contained *n*-nonane. However, inasmuch as dodecyl and tetradecyl alcohols are the principal constituents of "Lorol," the amount of hydrocarbon formed from any of the other alcohols present should be small.

[3] Wojcik and Adkins, This Journal, 55, 1293 (1933).

DEPARTMENT OF CHEMISTRY
JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

RECEIVED JUNE 7, 1933
PUBLISHED SEPTEMBER 5, 1933

COMMUNICATIONS TO THE EDITOR

PHOSPHOROUS FLUOROCHLORIDES

Sir:

We have found that the fluorination of PCl_3 by SbF_3 in the presence of $SbCl_5$[1] yields three gases, PF_3 in large amounts and two new gases, PF_2Cl boiling at approximately −48° and melting at approximately −166°, and small amounts of a $PFCl_2$ boiling a little below room temperature. These new substances are colorless both as gas and liquid, and fume in moist air. Variations of the experimental conditions indicate that the best yields are obtained when 450 parts of PCl_3 and 10 parts of $SbCl_5$ are vigorously stirred while sublimed SbF_3 is slowly added at room temperature.

The low yields by the above method caused us to try converting the PF_3 to the fluorochlorides. It was found that by passing an equimolecular gaseous mixture of PCl_3 and PF_3 through a glass tube filled with broken porcelain heated by an electric furnace so that the temperature of the exit gases was 200°, 50% of the mixture was converted to PF_2Cl and $PFCl_2$ in one pass. We are trying this same general method on mixtures of other non-polar chlorides and fluorides. The complete results of these investigations will be reported later.

[1] Booth and Swinehart, This Journal, 54, 4751 (1932).

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO

HAROLD SIMMONS BOOTH
ABE R. BOZARTH

RECEIVED JUNE 30, 1933 PUBLISHED SEPTEMBER 5, 1933

AN ATTEMPT TO PREPARE A CHLORIDE OR FLUORIDE OF XENON

Sir:

Frequent attempts have been made to prepare compounds of the noble gases with more electronegative elements, but the results have not been satisfyingly definite. Von Antropoff[1] has described briefly some experiments which indicate that krypton chloride and bromide exist, but no determinations of their composition and physical properties have been published. Both von Antropoff[1] and Pauling[2] have suggested that combination might possibly result with krypton or, more probably, with the heavier xenon. We have carried out experiments in which xenon was mixed with both chlorine and fluorine in an attempt to obtain these halides of xenon.

A mixture of xenon (70 mm.) and chlorine (225 mm.) contained in a quartz tube was irradiated with the light from a mercury arc in Pyrex and in quartz, and from a carbon arc. The source of light in all cases was placed close to the container. The pressure was measured by means of a Pyrex click gage attached through a graded seal to the quartz vessel. In no case was any pressure change observed during or at the end of a twelve-hour exposure. When the gas mixture was condensed by means of liquid air, a small amount of red solid was observed whose color disappeared shortly after removing the liquid air. The mixture was next transferred to a Pyrex bulb equipped with tungsten electrodes. After sparking for varying periods of time and then condensing the contents of the bulb with liquid air, larger amounts of the red solid noted above appeared. A number of tests showed that, in all probability, the red substance was the colored modification of hydrogen chloride described by Giauque.[3] Small amounts of hydrogen chloride are difficult to remove from chlorine and it was doubtless present as an impurity; some may have also been formed by the action of the highly activated chlorine on small amounts of water adsorbed on the walls of the vessel. No definite evidence for the presence of a xenon chloride was found.

It was found that fluorine, carefully freed from hydrogen fluoride, could be kept for an indefinite period in quartz bulbs which had been baked out under vacuum.[4] The small amount of silicon tetrafluoride and oxygen formed as the result of sealing the bulbs at long narrow capillary constrictions did not appear to promote any etching action. By means of quartz "break-offs" a mixture of some 600 mm. of fluorine and 30 mm. of xenon was prepared in an all-quartz apparatus provided with copper electrodes. On condensing the mixture in a side tube at −210° no visual evidence of the existence of anything except liquid fluorine and solid xenon was observed. When the refrigerant was removed the fluorine boiled away rapidly, leaving a volatile white solid with all the properties of xenon. A high voltage (30 k.v.) discharge was then passed through the mixed gases for varying intervals of time. The contents of the apparatus were con-

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(1) Von Antropoff, Weil and Frauenhof, *Naturwissenschaften*, **20**, 688 (1932).

(2) Private communication.

(3) Giauque, THIS JOURNAL, **50**, 101 (1928).

(4) See also von Wartenberg, Sprenger and Taylor, *Z. physik. Chem.*, Bodenstein Festband, 61 (1931).

densed out frequently, but the appearance and properties were no different from those observed before applying the discharge. It was noted that the side tube was appreciably attacked after some time, and this might be due to the action of a reactive xenon fluoride (compare rhenium hexafluoride) or to the presence of a small amount of moisture in the xenon. It cannot be said that definite evidence for compound formation was found. It does not follow, of course, that xenon fluoride is incapable of existing. It is known, for example, that nitrogen and fluorine do not combine in an electrical discharge, but when prepared indirectly nitrogen trifluoride is a very stable compound.

We are greatly indebted to Dr. F. J. Allen, who kindly supplied the xenon used in the experiments.

CONTRIBUTION NO. 371 FROM THE
GATES CHEMICAL LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

DON M. YOST
ALBERT L. KAYE

RECEIVED JULY 7, 1933 PUBLISHED SEPTEMBER 5, 1933

PREPARATION OF PURE 1-BUTENE AND ISOBUTENE

Sir:

Recently [*Compt. rend.*, **196**, 973 (1933)] Matignon, Moureu and Dode reported that pure aluminum oxide yields only 85% of 1-butene, the remainder being 2-butene.

This is not in agreement with the results previously obtained in our laboratories where it has been found that 1-butene without a trace of 2-butene can be prepared by the dehydration of *n*-butyl alcohol with aluminum oxide. The procedure is as follows: *n*-butyl alcohol is passed with a speed of 75 g. per hour through a glass tube (length, 50 cm.; inner diameter, 2 cm.), filled with 6–8 mesh aluminum oxide and maintained at a temperature of 375–425°. The butenes formed are collected and subjected to distillation in a low-temperature Podbielniak precision distilling apparatus [*Ind. Eng. Chem., Anal. Ed.*, **5**, 172 (1933)].

The aluminum oxide was prepared by the precipitation of aluminum nitrate with ammonium hydroxide; activated alumina received from Alcoa Ore Company, St. Louis, Missouri, gives 1-butene 99.6% pure.

The discrepancy between these results and those of Matignon, Moureu and Dode lies probably in the fact that these authors analyzed the product by converting it into dibromide and subjecting the dibromide to distillation. This method of analysis is not a very reliable one, since isomerization of dibromide can readily take place during the distillation.

V. N. Ipatiev [*Ber.*, **36**, 2011 (1903)] obtained pure isobutene by the dehydration of isobutyl alcohol using aluminum oxide. This work has

been repeated in our laboratories and isobutene 100% pure is obtained by this method.

RESEARCH AND DEVELOPMENT LABORATORIES
UNIVERSAL OIL PRODUCTS COMPANY
HERMAN PINES

RECEIVED JULY 24, 1933 PUBLISHED SEPTEMBER 5, 1933

REMARKS CONCERNING THE PAPER OF G. P. BAXTER AND C. M. ALTER "THE ATOMIC WEIGHT OF LEAD FROM KATANGA PITCHBLENDE"

Sir:

G. P. Baxter and C. M. Alter [THIS JOURNAL, **55**, 2785 (1933)] discuss the theory of the origin of the actinium series [Grosse, *Phys. Rev.*, **42**, 565 (1932)] on the basis of their careful and thorough experimental investigations of the atomic weight of uranium lead from Katanga pitchblende. They find that the lead extracted from the altered yellow portions of the mineral has a lower atomic weight than the lead from the original pitchblende and see in this fact a contradiction to the theory.

We consider that their findings support the theory and think the following the most plausible explanation of the facts.

It is usually considered by mineralogists and geologists [see for instance A. Holmes, "The Age of the Earth," pp. 207–217; G. Kirsch, "Geologie and Radioaktivitat," Chapter III] that lead is leached out from pitchblendes with much greater difficulty than uranium. This is due (1) to its much smaller concentration; (2) to the fact that it forms an insoluble uranate, and generally, because of its chemical nature, lead is much less soluble in acid and alkaline waters than uranium, which easily gives soluble uranyl complex salts. It is, therefore, natural to conclude that the uranium, leached out of the original mineral and redeposited in its veins and crevices, will be, to a great extent, free from U-Pb and being of a younger age, will produce, according to the actino-uranium theory, U-Pb containing less AcD and which therefore will have a lower atomic weight, as was actually found by Baxter and Alter. Furthermore, since this secondary uranium mineral is much more exposed to further leaching, its Pb/U ratio might be easily higher than the true ratio and lead to a wrong estimate of its age.

All of these considerations are only valid in the absence of ordinary lead. A strong indication that such is the case here is given by the low atomic weight figures of Baxter and Alter and is definitely proved by F. W. Aston's mass analysis of Katanga lead [*Nature*, **129**, 649 (1932)].

In conclusion we may state that the actino-uranium theory offers new possibilities for checking geological age determinations and elucidating the phenomena of leaching and other alterations of uranium minerals.

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A. v. GROSSE

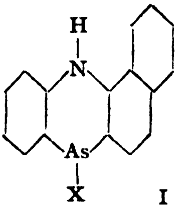
RECEIVED JULY 27, 1933 PUBLISHED SEPTEMBER 5, 1933

EVIDENCE FOR AN ASYMMETRICAL TRIVALENT ARSENIC ATOM

Sir:

The resolution of trivalent nitrogen compounds having three different substituent groups has long baffled organic chemists. Based on certain observations recorded in the literature, it would seem that when a molecule contains a nitrogen atom surrounded by three different groups and a lone pair of electrons, it should be asymmetrical, and capable of resolution if it contains the radicals usually employed for this purpose. Failure to accomplish this has been explained in several ways, one of which is that racemization is so rapid that the optically active molecule has too short a life. Assuming that the presence of additional shells of electrons around the kernel would tend to make a more stable arrangement, a properly constituted trivalent arsenic compound might be capable of resolution, thus showing that such a substance is asymmetrical.

7-Chloro-7,12-dihydro-γ-benzophenarsazine (Formula I, X = Cl) is such a substance. On treatment with silver *d*-bromocamphor sulfonate, dimers (A, B) having different rotations are obtained.



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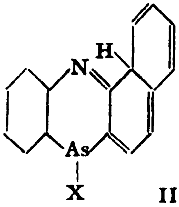

II

Subs.	Sp rot	Mol rot	Calcd. half life, min.	Calcd sp rot for As radical
A	+35.11°	+211.4°	70	−24.68°
B	+59.52°	+358.4°	36	+22.65°

Although the arsenic compound has not yet been regenerated from the camphor complex, the formation of these dimers indicates the presence of two asymmetric centers, one of which is in the camphor residue. Both the arsenic and nitrogen atoms are asymmetrical as represented, but since there is yet no recorded case of optical activity of compounds containing trivalent nitrogen, the activity in this instance is probably due to the arsenic. The existence of an asymmetric carbon atom, formed by a 1,3-shift of hydrogen (Formula II), though not excluded seems improbable.

McGILL UNIVERSITY
MONTREAL, CANADA
C. F. H. ALLEN
F. B. WELLS

RECEIVED JULY 31, 1933 PUBLISHED SEPTEMBER 5, 1933

ARSENATED DERIVATIVES OF PHENOBARBITAL

Sir:

An investigation of arsenated derivatives of phenobarbital undertaken several years ago in this Laboratory involves the use of 5-nitrophenyl-5-

ethylbarbituric acid and related compounds described by Bousquet and Adams [THIS JOURNAL, 52, 227 (1930)]. Through the Bart reaction, 5-aminophenyl- and 5-nitroaminophenyl-5-ethylbarbituric acids have been converted into the arsonic acids, 5-arsonophenyl- and 5-nitroarsonophenyl-5-ethylbarbituric acids. By means of hypophosphorous acid the latter were reduced to the corresponding arseno compounds.

During the research it became necessary to establish the position of the nitro group in the starting product and it was shown to be meta. In view of a recent article in this field [Rising, Shroyer and Stieglitz, *ibid.*, 55, 2819, footnote (1933)] in which mention is made of a forthcoming communication by Rising and Pierce concerning the structure of 5-nitrophenyl-5-ethylbarbituric acid, a brief outline is given here of the method of proof used in our work. 5-Nitrophenyl-5-ethylbarbituric acid (m. p. 279–280°) [all melting points are corrected] $\longrightarrow$ (nitrophenylethylmalonic acid) $\longrightarrow$ α-nitrophenylbutyric acid (80% yield, m. p. 115.5–116.3°; neutral equivalent 210, calcd. 209.1) $\longrightarrow$ *m*-nitrobenzoic acid (60% yield, m. p. 141–142°; identity confirmed by mixed m. p.).

5-*m*-Aminophenyl-5-ethylbarbituric acid was converted to a 5-(nitro-*m*-aminophenyl)-5-ethylbarbituric acid (dec. 330–340°) by the method of Bousquet and Adams, and by elimination of the amino group a new isomeric 5-nitrophenyl-5-ethylbarbituric acid (dec. 327–330°) was obtained. In the latter the nitro group may occupy the ortho or para position; the difficulty of hydrolyzing this compound has prevented us from establishing its structure.

BAKER LABORATORY OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

MILTON T. BUSH
JOHN R. JOHNSON

RECEIVED AUGUST 2, 1933 PUBLISHED SEPTEMBER 5, 1933

THE NITRATION OF PHENOBARBITAL

Sir:

As stated in a previous publication [THIS JOURNAL, 55, 2817 (1933)] the authors have proved that the nitration of phenobarbital

$$(C_6H_5)(C_2H_5)\underline{CCONHCONHC}{=}O$$

leads to the formation of 5-*m*-nitrophenyl-5-ethylbarbituric acid.[1,2] That the product of nitration of melting point 279–280° (corr.) is the meta, and not the para, isomer was proved as follows: 8.4 g. of the nitro-ureide yielded on oxidation 1.0 g. of *m*-nitrobenzoic acid, which was identified by

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(1) In confirmation of the findings of the present authors, Bush and Johnson have recently offered evidence for the formation of the meta rather than the para derivative

(2) It is of interest to note that the sulfonation of phenobarbital leads to a meta derivative. (Stieglitz and Yoran, unpublished dissertation for the doctorate degree, University of Chicago, June, 1933).

means of comparing its properties and those of the corresponding amino acid with the behavior of authentic samples of these substances. The nitrophenobarbital of melting point 279–280° must therefore be a *m*-nitro compound.

Residues obtained by evaporation of the alcohol used for purification of the crude nitration product will be examined for ortho and para nitro-derivatives.

GEORGE HERBERT JONES CHEMICAL LABORATORY
THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
MARY M. RISING
ALAN PIERCE

RECEIVED AUGUST 7, 1933 PUBLISHED SEPTEMBER 5, 1933

THE ACTION OF ELECTROLYTES ON WOOL FIBER

Sir:

During an x-ray investigation of the mordant dyeing of wool, an interesting phenomenon was observed. Using monochromatic radiation (Cu K_α) and mounting the fiber in a box type Laue camera in place of the usual crystal, pure wool fiber gives a very indistinct fiber diagram as contrasted with that obtained from the coarser keratin fibers [W. T. Astbury, *Trans. Faraday Soc.*, **29**, 193 (1933)] such as hair, quills and feathers. However, when this wool has been treated with certain electrolytes, two quite sharp and distinct rings appear. The inner ring is the more intense of the two, corresponding to a spacing of 4.08 Å., while the outer and lighter ring corresponds to a spacing of 3.72 Å. In the case of some of the wool samples, a broad ring quite close to the primary beam was observed corresponding to a spacing of 12.9 Å. Table I is a summary of the results obtained with all of the electrolytes that have been used. The third column indicates in a very approximate manner the visibility of the two lines (4.08 and 3.72 Å.) as observed on diagrams obtained after various treatments, relative to the type of treatment. It is interesting to note that wool which has been dyed as in a regular industrial process shows these two rings. The dye used throughout this work was commercial Orange II furnished through the courtesy of the Dupont Dye Company. NaX signifies the sodium salt of this dye. The wool fiber used was also furnished by the Dupont Dye Company.

It is suggested that the action of electrolytes, particularly those of an acid character, causes the wool protein to become crystalline to some extent and that these crystallites so formed are unoriented along the fiber axis as evidenced by the character of the rings. Table II shows the results of a calculation that would lead one to believe that these three rings are but high orders of a period of 77.8 Å. in length. The data in Table II are averages of all the observations made on many films. The rings on the

TABLE I

Nature of electrolyte	Treatment	Relative visibility of rings on diagram
NaX (5%)	Boiled 5 hours and rinsed in dist. water	Very good
NaX (5%)	Boiled 5 hours and washed 10 hours in boiling water	Faint but distinct
$AlCl_3$ (5%) and NaX (5%)	Boiled in $AlCl_3$ 2 hours, NaX 10 min. rinsed	Good
$CrCl_3$ (5%) NaX (5%) and HCl (1.5 *N*)	Boiled in $CrCl_3$ 30 min. NaX 10 min. (soln. 1.5 *N* HCl) boiled in water for 1 hour	Faint but distinct
$CrCl_3$ (5%) NaX (5%) HCl (1.5 *N*)	Boiled in $CrCl_3$ 2 hours NaX 10 min. rinsed (all solns. 1.5 *N* HCl)	Good
HCl (1 *N*)	Boiled 24 hours, rinsed	Very good
$HC_2H_3O_2$ (1 *N*)	Boiled 16 hours, rinsed	Very good
H_2SO_4 (0.5 *N*)	Boiled 16 hours, rinsed	Good
NaOH (3% of wool weight)	Boiled 3 hours, rinsed	Not definite but seems indicated
Na_2CO_3 (3%)	Boiled a few minutes until considerably decomposed	Not definite but seems indicated
NaCl (10%)	Boiled 16 hours, rinsed	Very faint
KI (10%)	Boiled 16 hours, rinsed	Good
$NaC_2H_3O_2$ (10%)	Boiled 16 hours, rinsed	Faint but distinct
Na_2SO_4 (1 *M*)	Boiled 16 hours, rinsed	Very faint
NaH_2PO_4 (1 *M*)	Boiled 16 hours, rinsed	Faint but distinct
$AlCl_3$ (1 *M*)	Boiled 5 hours, rinsed	Very faint
$AlCl_3$ (1 *M*)	Boiled 20 hours, rinsed	Faint but distinct
$AlCl_3$ (1 *M*)	Boiled 48 hours, rinsed	Good
Mordant and dye baths	Mordanted and dyed as in commercial process	Faint but distinct

various plates were precisely the same within the experimental error of measurement. Astbury gives 2.8 Å. as the length of a protein residue in wool. The length 77.8 Å. could be divided into 28 periods of 2.78 Å. each, which is very nearly Astbury's value for one protein residue.

TABLE II

Sin Θ	d ($n = 1$)	Intensity	Assumed n	$\frac{\sin \Theta}{n}$	% Deviation from average
0.05960	12.9	Strong	6	0.00993	+0.4
0.18824	4.08	Medium	19	.00991	+0.2
0.20677	3.72	Weak	21	.00985	−0.4

$$\text{Average } \sin \Theta/n = 0.00989$$

$$d = 1.54/(2 \times 0.00989) = 77.8 \text{ Å.}$$

CHEMICAL LABORATORY
JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

DONALD A. WILSON
NEIL E. GORDON

RECEIVED AUGUST 10, 1933 PUBLISHED SEPTEMBER 5, 1933

FREE PHENYL RADICALS IN THE GAS PHASE

Sir:

In the past few years a number of investigators have demonstrated the existence of active gaseous hydrocarbon molecules in experiments in which various types of substances were thermally decomposed. These have been called free radicals. So far only the methyl and ethyl radicals have been reported. In some experiments which we have been performing we have strong indications of the existence of the free phenyl radical in the gas phase.

The apparatus was made of quartz and consisted of a chamber to contain the lead tetraphenyl, a short region inside an electric furnace inclined slightly from the horizontal, a chamber to retain the liquid and crystalline products formed (chiefly diphenyl) and a chamber in which mercury was kept refluxing. The procedure was similar to that used in our work on the chemical reactions of gaseous methyl and ethyl [THIS JOURNAL, 55, 2696 (1933)]. The lead tetraphenyl was kept just below its melting point (215–220°) and the apparatus run for six hours at an indicated pressure of 0.01 mm.

The deposit formed in the mercury reflux chamber was recrystallized from alcohol. Among the characteristic broad crystals of diphenyl there appeared scattered needle-like crystals. Several were picked out and an attempt made to determine their melting point. This was in the region of 120° as near as could be determined with this small sample. The melting point of mercury diphenyl is 120°. A qualitative analysis showed mercury.

As neither lead tetraphenyl nor diphenyl reacts with mercury vapor, we believe that active phenyl radicals were present. Further work is in progress on this problem.

DEPARTMENT OF CHEMISTRY
DEPAUL UNIVERSITY, CHICAGO

M. F. DULL
J. H. SIMONS

RECEIVED AUGUST 16, 1933 PUBLISHED SEPTEMBER 5, 1933

THE FORMATION OF FREE RADICALS FROM ALIPHATIC AZO COMPOUNDS

Sir:

In view of the publication of a communication on this subject by Leermakers [THIS JOURNAL, 55, 3499 (1933)] it seems desirable to publish an account of some work we performed in this connection in August, 1931. We found that both azomethane and azoisopropane readily remove antimony mirrors when passed through a furnace heated in the range 450–550°; acetone was used as the carrier gas. The temperature of the furnace was far too low to cause any perceptible decomposition of the acetone.

At that time we were more particularly interested in azoisopropane because it seemed to offer the possibility of preparing the free isopropyl group. Paneth and his co-workers [*Ber.*, **62**, 1335 (1929); **64**, 2702, 2708 (1931)] had already prepared free methyl and ethyl but had failed to obtain the *n*-propyl or the isobutyl radicals from the corresponding lead compounds; they concluded that a large proportion of the *n*-propyl and isobutyl radicals must have decomposed into methyl groups since zinc dimethyl was identified among the products. It occurred to us, however, that the isopropyl and tertiary butyl radicals should have about the same stability as the ethyl radical, since in all three cases a C–H bond must break in order for the radical to decompose with production of an olefin hydrocarbon, whereas all other paraffin radicals can undergo this decomposition by rupture of a C–C bond. This may be easily seen from the examples given in a previous paper [Rice, THIS JOURNAL, **55**, 3036 (1933)].

We first made some measurements of the rate of disappearance of the active fragments according to the method described by Rice, Johnston and Evering [THIS JOURNAL, **54**, 3529 (1932)]. The following table gives the results obtained with a 1% solution of azoisopropane in acetone, using a quartz tube 0.4 cm. in diameter and an acetone pressure at the standard mirror of 0.22 mm. of mercury; the fall in pressure down the tube was 0.007 mm. per cu.

d, cm.	15	22	11	30	25	18	13	28	20	30	24
t_m, sec.	51	118	33	225	275	71	42	275	83	305	270

d is the distance from the furnace to the standard mirror and t_m is the time of removal of the standard mirror. These results were plotted and compared with the curve obtained for lead tetramethyl under identical conditions. The first parts of the two curves coincide exactly, but at distances greater than 20 cm. from the furnace the concentration of active fragments does not fall off as rapidly in the case of azoisopropane as in the experiments with lead tetramethyl. This behavior would seem to indicate the formation of a fragment of comparatively long life during the decomposition of azoisopropane. However, at that time we had not yet developed any convenient method of identification and therefore could not determine conclusively whether the isopropyl group was formed, perhaps undergoing partial decomposition into propylene and atomic hydrogen.

JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
F. O. RICE
B. L. EVERING

RECEIVED AUGUST 19, 1933 PUBLISHED SEPTEMBER 5, 1933

INDIUM AND SCANDIUM IN PEGMATITE

Sir:

Indium and scandium have been found in a pegmatite dyke in Western Utah. Analyses of samples taken at random along the dyke indicate 1.0–2.8% indium and 0.5–1.2% scandium.

It is interesting to note that these metals do not occur in connection with zinc. The chief minerals of the deposits are cordierite, actinolite, antigorite, calcite and molybdenite. Apparently the indium occurs as a partial replacement of aluminum in cordierite. The mode of occurrence of the scandium has not yet been determined.

We have succeeded in developing a method for extracting the scandium. This method will be described shortly in detail (as a contribution from the Chemical Laboratory of the University of Utah).

SALT LAKE CITY, UTAH HENDRIK ROMEYN, JR.

RECEIVED AUGUST 24, 1933 PUBLISHED SEPTEMBER 5, 1933

NEW BOOKS

Annual Survey of American Chemistry. Volume VII, 1932. Edited by Clarence J. West, Director, Research Information Service, National Research Council. Published for National Research Council by the Chemical Catalog Company, Inc., 330 West 42d Street, New York, 1933. 346 pp. 13.5 × 21.5 cm. Price, $4.00.

In this volume of the Annual Survey a new policy in regard to the selection of subjects to be considered has been put into effect. The plan followed involves the reduction in the number of fields covered in any year and the treatment of the less important topics once in two or three years. This change was made necessary as the result of the growing size of the volumes from 257 pages in the first year to 543 pages in the sixth year. The number of chapters has been reduced from 37 to 27, which cover 346 pages. Although several topics have been eliminated, the work covered is so extensive that on the average eight references are considered per page, with the result that the discussions are exceedingly brief and limited often to not more than a statement of the titles. Notwithstanding this fact the authors, in general, have produced readable articles which give a clear impression of the recent developments in the subjects treated. The volume is an example of the art of condensation in scientific writing, which is becoming more and more necessary as time goes on and production increases. Since the number of chapters has been reduced it appears to be desirable to list the subjects treated in this volume. They are as follows: theories of solution, kinetics of homogeneous gas reactions, subatomic phenomena, thermodynamics and thermochemistry, colloids, contact catalysis, aliphatic compounds, carbocyclic compounds, heterocyclic compounds, biochemistry, photochemistry, x-ray examination of materials, electrochemical practice, inorganic chemistry 1929–1932, non-ferrous metals, foods, fermentation, water, sewage and trade wastes, soils and fertilizers, coal, petroleum chemistry and technology, textile fibers, dyes and dyeing, rubber, synthetic plastics, chemical engineering. It should be noted that chemical engineering appears for the first time in the Annual Survey. The inclusion of this topic will add to the value of the book.

The Survey has proved of particular value to those who cannot find time to read extensively. It makes it possible for a chemist to learn with little effort something of the developments outside of his own field.

JAMES F. NORRIS

Elementary Quantitative Analysis. Theory and Practice. By HOBART H. WILLARD, Ph.D., Professor of Analytical Chemistry, University of Michigan, and N. HOWELL FURMAN, Ph.D., Associate Professor of Chemistry, Princeton University. D. Van Nostrand Company, Inc., 250 Fourth Ave., New York, 1933. viii + 406 pp. Illustrated. 14.5 × 22.5 cm. Price, $3.25.

This book should be welcomed by all chemists interested in the teaching of quantitative chemistry. It can be characterized as quantitative analysis *per se*, not a pre-professional hurdle nor preliminary practice in technical analysis. The practice determinations are well selected, varied in nature, and in such numbers that flexibility is allowed the teacher in choice of exercises. Recent developments in quantitative methods are introduced through appropriate exercises and combined with the best of well-established, long-standing methods. Directions are written in a simple straightforward style that will impress the student with the essentials of the processes being carried out.

However, the book is more than a collection of conventional directions for carrying on specific determinations designed to familiarize the student with quantitative technique. It is especially characterized by a generous amount of space devoted to the fundamental theory of quantitative chemical processes. In a series of chapters, judiciously distributed among chapters of practical laboratory directions, the modern theoretical basis of analytical chemistry is simply but thoroughly discussed. This material is a natural continuation of the general theory of the introductory course and of quantitative analysis. Many teachers, whose training was secured more than a decade ago, will find interesting information in these theoretical chapters.

Fundamentally sound as the book is, the reviewer cannot but express regret that the authors did not continue to use their original order of treatment; that is, place gravimetric processes before volumetric. This order seems to be the more logical and more in accord with the nature of this text. To be sure, the order of treatment used is well connected and teachable, but it has been the hope of the reviewer that one good quantitative analysis might continue to place first things first, and resist the demand for pre-professional short courses, that is, for the teaching of applications before the fundamentals are thoroughly presented.

With regard to detailed criticisms few objections can be raised. The work is well written and printed throughout, although reading the preface might not seem to promise this, as, in the second paragraph, there is an error in printing and a split infinitive. The authors have included a number of problems and review questions but not too many, and more discussion of methods of solving quantitative problems, the use of reference tables, handbooks, slide rules, etc., might be included. Since some students are familiar with proton chemistry, mention of Brönsted's concepts might have been included in Chapter VI.

The authors have avoided specifying complicated or highly specialized apparatus and only occasionally references are made to specific forms of conventional apparatus or materials. This is commendable since such practical details are administered differently in different laboratories. For example, the reviewer would not agree that the type of buret described and illustrated is the best even for general use, or that a certain excellent rubber paint is the preferred method of lining standard alkali bottles.

There are admittedly other details, described in the book, on which opinions differ, but they are after all mere details. The general impression remains that the authors have produced a thoroughly good textbook of elementary quantitative chemistry, commendable both as to teachability and scope of information presented.

C. R. HOOVER

Der Glaszustand. (The Glassy State.) By GUSTAV TAMMANN, Göttingen. Verlag von Leopold Voss, Salomonstrasse 18 B, Leipzig C 1, Germany, 1933. 123 pp. 86 figs. 16 × 23.5 cm. Price, RM. 8.70.

In this monograph there are collected and reviewed the results of numerous researches by Professor Tammann and his students upon substances in the glassy state together with some of the related work of others in the same field. A complete review of the field would be impossible in a book of this size. Consequently the plan is adopted of presenting first in each chapter the author's work upon a phase of the subject and then concluding with a consideration of the parallel work of others, where such work exists. This monograph is unique among books upon glass in that attention is wholly directed to the scientific aspects of the subject with almost no reference to the practical side of glass manufacture.

Because of this point of view, the glasses which were studied were chosen rather because of their suitability for the investigation to be carried out than because of their practical utility. Most of the work was done upon organic glasses softening between 0 and 100°, but the author states that the general results may be carried over into the field of the technically important silicate glasses where the higher temperatures required greatly increase the experimental difficulties encountered.

After a brief review of work upon the formation of crystallization centers and the linear rate of crystallization in supercooled liquids, which will be familiar to most readers, the first half of the book is devoted to a discussion of the changes which occur in all the physical properties of a glass as its temperature is increased through the interval in which it softens. It is shown that for normal glasses the physical properties in general undergo rapid but continuous changes in the interval between the temperature at which the glass ceases to be brittle and that at which it can first be drawn out into threads. In this section is discussed also some most interesting work upon the behavior of glasses under high pressures.

The last half of the book does not possess the unity of the first half but treats a number of more or less unrelated topics. For the most part it is devoted to a further consideration of the phenomena of crystallization or devitrification. There are, however, chapters upon the relation between the properties of the glassy state and the crystalline state, upon the increase in the strength of glass threads with decreasing size, upon the induced birefringence of glass surfaces, upon the molecular constitution of glasses, and upon irreversible changes in the physical properties of glasses. It is perhaps worthy of special mention that condensation and polymerization products such as Bakelite and polyisoprene are found to be distinctly "abnormal" glasses.

While this book contributes nothing directly to the technology of glass it may be recommended highly to those having a scientific interest in this state of matter. It should prove most suggestive to those engaged in the study and development of silicate glasses and should be valuable to the general student as shedding light on what is probably the most obscure realm of physical chemistry.

C. H. GREENE

Phase Rule Studies. An Introduction to the Phase Theory. By J. E. WINFIELD RHODES, Lecturer in Physical Chemistry, Municipal Technical College, Blackburn. With an introduction by E. L. RHEAD, Lecturer in Metallurgy and Assaying in the University and College of Technology, Manchester, England. Oxford University Press, 1933. x + 131 pp. 58 figs. 13 × 19 cm. Price, $2.25.

This is a somewhat elementary though entirely scientific presentation of the whole field of the phase rule, including the treatment of four-component systems. In order to secure such a breadth of field, it has been necessary to make some sacrifices in depth.

The introduction indicates that the book is intended to bridge the gap for students whose knowledge of the subject has come from the brief study usually given it as a part of their physical chemistry, but who find that they need something more extensive upon taking up mineralogical or metallurgical investigations. The book will certainly do something of real value for such students, though it just as certainly leaves much reading to be done. A number of the systems taken for discussion are of mineralogical interest and not previously available in textbooks. The presentation is clear and in good form.

ARTHUR E. HILL

Chemische Grundlagen der Lebensvorgänge. Eine Einführung in biologische Lehrbücher. (The Chemistry of Living Processes. An Introduction to Biological Literature.) By Professor CARL OPPENHEIMER, Dr. Phil. et Med., Berlin. Georg Thieme Verlag, Antonstrasse 15/19, Leipzig C 1, Germany, 1933. vii + 298 pp. 1 fig. 17 × 25 cm. Price, M. 22.50; bound, M. 24.50.

In the preface the author states that this work was originally planned to appear in two parts, "Chemie der Zellvorgänge" and "Energetik der lebenden Substanz" to supplement the recent "Lehrbuch der allgemeinen Physiologie" by Ernst Gellhorn. This plan, however, was later changed because the author wished to appeal to a somewhat wider audience than simply animal physiologists. The present volume is directed not only at zoölogical and medical problems but the author hopes that it will prove of equal value to botanists and bacteriologists.

The book is divided into five parts: (I) Living Substance as a Chemical System, comprising sixteen pages and considering briefly a short introduction in which the composition of protoplasm is considered, followed by a discussion of the elements which occur in living cells.

II. Chemical Compounds in Protoplasm, comprising a short discussion of colloids, association, molecular size, etc., and followed by brief considerations of some of the more important characteristics of the fats and waxes, the carotinoids and the phospholipides, the carbohydrates, the respiratory pyrrole-containing pigments and the proteins.

III. Anabolism and Catabolism, including carbon and nitrogen assimilation and changes which organic compounds undergo in living cells.

IV. The Chemical Mechanism of Cell Activity, in which attention is called to the role of enzymes in biological processes.

V. The Energy Process of Living Substance, in which are considered the general nature of energy transfer and energy cycles, followed by a discussion of living substance as a chemico-dynamical machine.

The volume closes with an adequate subject index.

As might be expected from a knowledge of the field of interest of the author, the major emphasis in this volume is devoted to enzyme chemistry. Almost two-thirds of the book may be regarded as a condensed consideration of enzyme reactions, so that those workers who do not have access to the author's extensive (and expensive) "Die Fermente und ihre Wirkungen" can here find a very excellent, and adequate, résumé of Oppenheimer's views on enzymes, their reaction and the role which they play in vital processes. This is the chief value of the book. The brief introductory discussions of proteins, carbohydrates, fats, etc., are so brief as to contribute little that is new or unique and serve only to introduce the later portions dealing with enzymes and their reactions. Few persons are better qualified than is Oppenheimer to discuss enzym and their reactions and it is this discussion which appeals to the reviewer and which he feels justifies the addition of the present volume to the mass of biochemical texts.

ROSS AIKEN GORTNER

Chemistry of Food and Nutrition. By HENRY C. SHERMAN, Ph.D., Sc.D., Mitchill Professor of Chemistry, Columbia University. Fourth edition, rewritten and enlarged. The Macmillan Company, 60 Fifth Ave., New York, 1932. xiii + 614 pp. 14 × 20.5 cm. Price, $3.00.

The fourth edition of this standard work has been very largely rewritten and somewhat enlarged to include the most recent advances in biochemistry and nutrition. Separate chapters are now devoted to iron, copper and iodine, and to vitamins A, B, G, C, D and E. The chapter on "Dietary Standards" is especially to be commended for the well-balanced treatment it gives this controversial field.

CARL L. ALSBERG

BOOKS RECEIVED

July 15, 1933–August 15, 1933

K. F. BONHOEFFER AND P. HARTECK. "Grundlagen der Photochemie." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 295 pp. RM. 24; bound, RM. 25.

ERWIN B. KELSEY AND HAROLD G. DIETRICH. "Laboratory Manual to Accompany 'Principles of General Chemistry.'" Revised edition. The Macmillan Company, 60 Fifth Ave., New York. 133 + 73 pp. $1.50.

MARTIN KRÖGER, Editor. "Grenzflächen-katalyse." Verlag von S. Hirzel, Königstrasse 2, Leipzig, Germany. 387 pp. RM. 10.59; bound, RM. 12.50.

JULIUS SCHMIDT. "Lehrbuch der Organischen Chemie." Vol. XIX, 1932. Verlagsbuchhandlung Franz Deuticke, Helferstorferstrasse 4, Wien, Austria. 360 pp. M. 36, öst. S. 54; bound, M. 39, öst. S. 58.50.

J. E. VERSCHAFFELT. "Thermostatica." De Sikkel, Antwerpen, P. Noordhoff, N. V., Groningen-Batavia. 472 pp.

HARRY BOYER WEISER. "Inorganic Colloid Chemistry." Vol. I. The Colloidal Elements. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 389 pp. $4.50.

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 55 OCTOBER, 1933 NUMBER 10

Definitive Report of the Commission on the Reform of the Nomenclature of Organic Chemistry

Translation with

Comments

BY AUSTIN M. PATTERSON

Introduction

It is possible in the domain of organic chemistry to give several names to the same compound. This state of affairs has on the one hand the great advantage of permitting clear expression of thought and of rendering it easier to bring out analogies in structure wherever this is useful. But on the other hand the multiplicity of names for the same substance constitutes a serious obstacle in the preparation of indexes.

Translator's Note.—This report was unanimously adopted by the Commission and by the Council of the International Union of Chemistry at the meeting of the Union, held in Liége, September 14–20, 1930, and the official French text appears in the "Comptes rendus" of that meeting. It seemed likely that some details might be modified at the meeting scheduled to be held in Madrid in April, 1932, but as that meeting was postponed the report may be considered to have reached a certain stage of completion.

The rules are based on those of the Geneva Congress of 1892,[1,2] but include many changes and additions. They are naturally compromises in some cases, but are believed to represent a distinct advance in nomenclature practice.

Many of the provisions are already being observed in the publications of the American Chemical Society. It will be the policy of *Chemical Abstracts*, which was represented on the Working Committee by the translator, to put the rules into practice in its indexing to as great an extent and within as short a time as its long-established system of nomenclature and the requirements of its decennial indexes permit. The *Journal of the American Chemical Society* follows, in general, the usages of *Chemical Abstracts*.

The translator acknowledges his indebtedness to the valuable comments of Professor P. E. Verkade,[3] some of whose examples he has used.

The text of the report is given in ordinary type; comments by the translator are in small type.

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(1) Pictet, *Arch. sci. phys. nat.*, [3] **27**, 485–520 (1892)

(2) Tiemann, *Ber.*, **26**, 1595–1631 (1893).

(3) Verkade, *Rec. trav. chim.*, **51**, 185–217 (1932).

This difficulty was experienced as long ago as 1892 and the celebrated Congress of Geneva, at which thirty-four of the best qualified chemists from nine countries of Europe created the Geneva nomenclature, attempted to remedy it by laying down as Rule 1 of its report the following: "In addition to the customary methods of nomenclature there shall be established for each organic compound an official name, which will enable it to be found under only one entry in indexes and dictionaries." As is generally known, this intent of the Geneva Congress has not been realized. The Geneva nomenclature has not been sufficiently worked out except for acyclic compounds. Even for many of these, and still more for the rest, its application gives names which are much too complicated. This is probably the reason why the commission of 1892 did not complete its work.

Today, an official nomenclature for indexes, which was desirable forty years ago, has become quite unnecessary for the following reasons: (1) In 1918 a new edition of Beilstein commenced to appear; this admirable work facilitates bibliographic researches in an extraordinary manner.

(2) The problem has been solved by the formula indexes which are now in use in a number of chemical journals, including *Chemical Abstracts* and *Chemisches Zentralblatt.*

Nevertheless, the Geneva nomenclature has been of much value to organic chemistry, for its fundamental ideas are of great importance from the systematic standpoint throughout the entire extent of the science. The classification in Beilstein is based upon it for this reason.

As has just been observed, the Geneva names are inconvenient in the majority of cases and not very practical for ordinary use. The editors of Beilstein as well as of other compilations have rightly employed them, not alone but with the addition of the names in current use.

Now, a revision of these names has become more and more pressing; for the number of compounds has increased incessantly to an extraordinary degree and their discoverers, although following usage as far as possible, have not always made a happy choice of names and have even, in some cases, adopted names manifestly incorrect.

In order to remedy this regrettable state of affairs, in 1922 the International Union of Chemistry, on the proposal of Sir William Pope, named a Working Committee (Comité de Travail) to study the reform of the nomenclature of organic chemistry, composed of delegates from the editorial staffs of important chemical journals. The following were chosen as members: Messrs. Crane, Greenaway and Marquis, representing *Chemical Abstracts*, the *Journal of the Chemical Society* of London and the *Bulletin de la Société Chimique de France.* This Committee was instructed to make a report and submit it to the Commission of the Union, which approved it. The following year this Committee was enlarged by representatives of the *Gazzetta chimica italiana* (Paternò), *Helvetica Chimica*

Acta (Pictet) and *Recueil des travaux chimiques des Pays-Bas* (Holleman). The last-named was chosen chairman, and M. Marquis secretary.

In the course of time this Committee underwent the following changes: Mr. Crane was replaced by Mr. Patterson, Mr. Greenaway (assisted by Mr. Gibson) retired and was replaced by Mr. Barger. M. Paternò was presently replaced by M. Peratoner, but illness prevented him from participating in the sessions. After his death, the Italian Chemical Society named M. Mario Betti, who was unable to take part in editing the report but was present at the Eighth Conference at Warsaw in 1927, the Ninth at The Hague (1928) and the Tenth at Liége (1930) in which the said report was discussed and in part modified. Herr Prager, editor of Beilstein, named by the Verband deutscher chemischer Vereine as its representative on the Committee, was also present at Liége.

During the years 1924–1928 the Committee held several meetings in Paris; the result of its work was a report which was presented at The Hague in 1928 to the Commission of the Union on the reform of the nomenclature of organic chemistry. The latter proposed certain modifications which were examined again by the Working Committee. The report as thus amended was discussed at the meeting of the Commission in 1930 at Liége and was then adopted unanimously.

This report is not intended to interfere with the editing of Beilstein or of *Chemical Abstracts*, publications which have followed for many years their own systems of nomenclature, which moreover are very similar to the rules now adopted.

The object of the Committee in its work has been rather to follow usage as nearly as possible (see rule 1 below), to record it while at the same time proposing certain simplifications and eliminating incorrect names. It hopes that the flexible system of nomenclature thus created will be used more and more by authors of articles and of treatises on organic chemistry as well as in oral instruction and that the editors of journals will recommend its use as far as possible.

Rules

Index: I. General. II. Hydrocarbons: 1. Saturated Hydrocarbons. 2. Unsaturated Hydrocarbons. 3. Cyclic Hydrocarbons. III. Fundamental Heterocyclic Compounds. IV. Simple Functions. V. Complex Functions. VI. Radicals. VII. Numbering.

I. General

1. As few changes as possible will be made in terminology universally adopted.

The Committee members were apparently agreed that any attempt to introduce sweeping changes in terminology, however consistent they might be, would prove impractical and undesirable in the present stage of the science. The purpose of the rules, therefore, is rather to unify existing practice as far as possible by eliminating objectionable names and guiding future naming along desirable lines. The proposal (in Geneva rule 1) of an official name for each organic compound has been abandoned.

2. For the present, only the nomenclature of compounds of known constitution will be dealt with; the question of substances of imperfectly known constitution is postponed.

It is evident that a special technique is required for naming compounds of incompletely known structure so as to denote the presence, or the removal, of certain atoms or groups, or relation to other compounds. Although there might be an advantage in regularizing nomenclature practice in this field, the Committee decided not to consider it for the present. Moreover, the classification and naming of such important natural substances as the proteins and their derivatives, the lipides or lipoids, and the carbohydrates, were already in the hands of the Committee on Biochemical Nomenclature. The wording of this rule is identical with that of Geneva rule 2.

3. The precise form of words, endings, etc., prescribed in the rules should be adapted to the genius of each language by the subcommittees.

The wisdom of this rule seems evident, otherwise chemical word elements might conflict with important grammatical or other usages. As a sample of such difficulties may be cited the fact that in German -e is a case ending and hence -ene is not appropriate as a hydrocarbon suffix; it becomes -en instead. In Spanish the same ending becomes -eno. Most such adaptations will be made readily enough; a few, because of their newness, may require some ingenuity.

II. Hydrocarbons

4. The ending *ane* is adopted for saturated hydrocarbons Open-chain hydrocarbons will have the generic name *alkanes*.

The name "alkane" is better and shorter than "paraffin," especially since the latter term is now so commonly applied to a solid mixture.

5. The present names of the first four normal saturated hydrocarbons (methane, ethane, propane, butane) are retained. Names derived from the Greek or Latin numerals will be used for those having more than four atoms of carbon.

The words "or Latin" have been added to the Geneva rule (no. 4) because *nonane* is almost universally used for C_9H_{20} instead of the Greek derivative *enneane* (as also is *nona-* instead of *ennea-* in combination, as in *nonadecane*); and because *undecane* appears oftener than *hendecane*, although the latter has a respectable standing. For most of the alkanes, however, names of Greek derivation are customary.

6. Branched-chain hydrocarbons are regarded as derivatives of the normal hydrocarbons; their names will be referred to the longest normal chain present in the formula by adding to it the designations of the side chains. In case of ambiguity, or if a simpler name would result, that chain which admits of the maximum of substitutions will be selected as the fundamental chain.

This rule may require further interpretation. The version published by the Journal of the Chemical Society[4] is quite different. It reads: "Branched-chain hydrocarbons

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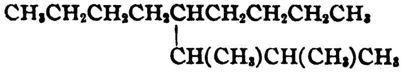
(4) *J. Chem. Soc.*, 1607–1616 (1931).

are regarded as derivatives of normal hydrocarbons; their names will be determined by the longest chain containing the maximum number of double or triple linkings (preference being given to the double linking where ambiguity arises), or, in the case of saturated hydrocarbons, by the longest chain in the formula. In cases where there might be doubt as to the choice of the longest chain, that one will be selected which admits of the maximum of substitution." It was the impression of the writer that this version, which he considers preferable, was adopted at Liége, but he has followed the French version of the "Comptes rendus" of the meeting.

If the French version is accepted, then it seems best to interpret it as referring to *saturated* hydrocarbons only, unsaturated hydrocarbons being treated in rules 8–10. The phrase "or if a simpler name would result" ("ou si cela donne un nom plus simple" in the French version) is of doubtful value as there may be differences of opinion as to which name is "simpler." In saturated branched-chain hydrocarbons, in the writer's opinion the longest chain present should be chosen as the fundamental one, and if there are two or more choices for the longest chain, then that one should be chosen in which there is the greatest number of substitutions (the reason being that the substituting radicals, while more numerous, will be of simpler structure).

Example:



$$CH_3CH_2CH_2CH_2\underset{\displaystyle CH(CH_3)CH(CH_3)CH_3}{\underset{|}{C}}HCH_2CH_2CH_2CH_3$$

By the principle of the "longest chain" the name would be 5-(1,2-dimethylpropyl)-nonane; but according to the rule the name 4-butyl-2,3-dimethyloctane (which avoids a branched side chain) is the one to be chosen if it seems simpler.

7. In case there are several side chains, the order in which such chains are named will correspond to the order of their complexity. The chain having the greatest number of secondary and tertiary atoms will be considered the most complex. The alphabetic order may also be followed in such cases.

The Committee members were divided in their preferences between an order of radical names based on structure (for example, one based on increasing weight, as methyl, ethyl, butyl) and an alphabetic order as used, for example, in *Chemical Abstracts*. The two possibilities were hence left side by side, not only in this rule but also more generally in rule 63.

The advocates of the structural basis for such an order did not formulate any complete rule, and the wording of rule 7 is not very clear. In the writer's opinion it means that the name of the hydrocarbon radical of lowest weight is to be announced first, then that of the next highest weight, and so on, and that as between isomers the normal radical comes first, then the ones of branched structure, *e. g.*, methyl, ethyl, propyl, isopropyl, butyl, isobutyl. The rule does not decide completely between branched isomers, and neither this rule nor rule 63 prescribes any structural order for the host of substituting groups which are not hydrocarbon radicals (such orders have been constructed, however).[5]

The beauty of the alphabetic order is that it furnishes a means of arranging in order, almost instantly, substituents of any kind. Its only difficulty is that a few radical names differ substantially in spelling in certain languages (*e. g.*, ethyl, Äthyl). In such cases a transposition would be necessary in the translation. Fortunately, the exact order of prefixes in an organic name is not of great importance except in indexes. Example of the alphabetic order: butyl, ethyl, isobutyl, isopropyl, methyl, propyl.

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(5) See for instance Stelzner, *Literatur-Register der organischen Chemie*, 1, xxiv–xxxiii (1913); 2, xxii–xl (1919).

(Or, if *iso-* is italicized, butyl, *iso*-butyl, ethyl, methyl, propyl, *iso*-propyl.) For further illustrations the indexes to *Chemical Abstracts* may be consulted.

8. In the names of open-chain unsaturated hydrocarbons having one double bond the ending *ane* of the corresponding saturated hydrocarbon will be replaced by the ending *ene;* if there are two double bonds, the ending will be *diene,* etc. These hydrocarbons will bear the generic names *alkenes, alkadienes, alkatrienes,* etc. Examples: propene, hexene, etc.

This rule follows the Geneva system and in addition introduces the generic names *alkene,* etc., corresponding to *alkane.* Strictly interpreted, it calls for the replacement of *ethylene* by *ethene.* The writer doubts if this change will ever become general but the higher names, as propene, butene, etc., seem to be slowly supplanting the older propylene, butylene, etc. Examples: $\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_3$, propene; $\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$, 1-butene; $\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H{=}\overset{5}{C}H\overset{6}{C}H_3$, 2,4-hexadiene. The double bond receives its number from the lowest-numbered carbon atom to which it is attached. The principle of "lowest numbers" (see rule 64) is always applied; for instance, 1-butene might also be called 3-butene, but the lower number is selected.

For the naming of branched unsaturated hydrocarbons see the comments on rule 10.

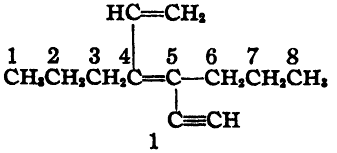
9. The names of triple-bond hydrocarbons will end in *yne, diyne,* etc. They will bear the generic name *alkynes.* Examples: propyne, heptyne, etc.

The Geneva ending *-ine* for these hydrocarbons has been replaced by *-yne* because -ine is reserved for names of organic bases (see rule 33). The English pronunciation of -yne is like that of -ine in "wine." It seems unlikely that the time-honored "acetylene" will be replaced by "ethyne" but the names for the higher members, such as propyne, ($\overset{1}{C}H{\equiv}\overset{2}{C}{-}\overset{3}{C}H_3$), 1-butyne ($\overset{1}{C}H{\equiv}\overset{2}{C}{-}\overset{3}{C}H_2\overset{4}{C}H_3$) and 2,4-hexadiyne ($\overset{1}{C}H_3\overset{2}{C}{\equiv}\overset{3}{C}{-}\overset{4}{C}{\equiv}\overset{5}{C}\overset{6}{C}H_3$) will probably be increasingly used.

10. If there are both double and triple bonds in the fundamental chain the endings *enyne, dienyne,* etc., will be used. The generic names of these hydrocarbons will be *alkenynes, alkadienynes,* etc.

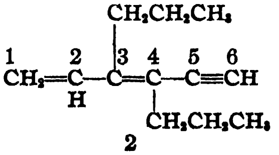
The endings *-enyne* and *-dienyne* given in the rule indicate that the double bonds are always to be expressed first, then the triple bonds. *E. g.,* $\overset{1}{C}H{\equiv}\overset{2}{C}{-}\overset{3}{C}H{=}\overset{4}{C}H\overset{5}{C}H{=}\overset{6}{C}H\overset{7}{C}{\equiv}\overset{8}{C}H$, octa-3,5-diene-1,7-diyne.

If we interpret rule 6 as applying to saturated hydrocarbons only (see the comments on rule 6), then the Committee has made no rule for the naming of *branched unsaturated* hydrocarbons. Two alternatives seem to be open: (1) to follow the Geneva system and choose the longest chain in the molecule as the fundamental one, even if it does not contain the double or triple bonds. (2) To consider the unsaturated linkages as functions (they are so listed in rule 52) and, guided by rule 18, to select as the fundamental chain that one which contains the maximum of double and triple bonds (even if it is not the longest present in the molecule). Example:



$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{\overset{HC=CH_2}{|}}{\overset{4}{C}}{=}\underset{\underset{C\equiv CH}{|}}{\overset{5}{C}}{-}\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_3$

1



$\overset{1}{C}H_2{=}\underset{H}{\overset{2}{C}}{-}\overset{\overset{CH_2CH_2CH_3}{|}}{\overset{3}{C}}{=}\underset{\underset{CH_2CH_2CH_3}{|}}{\overset{4}{C}}{-}\overset{5}{C}{\equiv}\overset{6}{C}H$

2

By method (1): 4-ethenyl-5-ethynyl-4-octene. By method (2): 3,4-dipropyl-hexa-1,3-dien-5-yne. (As to beginning the numbering with the double instead of the triple bond, see rule 64.) For general use the writer favors method (2) as being in accordance with the treatment of other functions, and also as better expressing the nature of the hydrocarbon in the ending of the name.

11. Saturated monocyclic hydrocarbons will take the names of the corresponding open-chain saturated hydrocarbons, preceded by the prefix *cyclo*. They will bear the generic name *cycloalkanes*.

The Geneva names *cyclopropane*, *cyclobutane*, etc., have won general acceptance, replacing the older names trimethylene, tetramethylene, etc. The latter names have a better use as applied to bivalent radicals (recognized in rule 57).

12. When they are unsaturated, rules 8–10 will be applied. However, in the case of partially saturated polycyclic aromatic compounds the prefix *hydro*, preceded by *di-*, *tetra-*, etc., will be used. Example: dihydroanthracene.

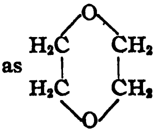
Further examples: cyclobutadiene, cyclohexene (not tetrahydrobenzene), 1,2-dihydronaphthalene. For completely saturated polycyclic aromatic hydrocarbons it was at one time proposed in the Committee to use the ending -ane; *e. g.*, naphthalane. This provision was later rejected, however. In so doing the Committee no doubt intended that "decahydronaphthalene" be used instead of "naphthalane," and so for other cases. It was therefore probably an oversight that the words "or wholly" were not added after "partially" in revising the rule.

13. Aromatic hydrocarbons will be denoted by the ending *ene* and will otherwise retain their customary names. However, the name *phene* may be used instead of *benzene*.

The best usage in English already conforms to this rule, which will help to hasten the disuse of such names as benzol, toluol and xylol for chemical individuals. "Phene," while logically related to "phenol," is not likely to replace "benzene."

III. Fundamental Heterocyclic Compounds

14. The endings of customary names, endings which do not correspond to the function of the substance, will undergo the following modifications, so far as they are in accord with the genius of each language: (a) The ending *ol* will be changed to *ole*. Example: pyrrole. (b) The ending *ane* will be changed to *an*. Example: pyran.

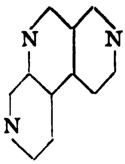
The change from *-ol* to *-ole* is obviously for the purpose of reserving -ol as an ending for the names of alcohols and phenols; similarly, the change from *-ane* to *-an* is made in order to reserve -ane for saturated parent compounds. The rule does not state whether names of fully saturated heterocyclic parent compounds such as  are to be spelled -ane or -an (*Chemical Abstracts* calls the above 1,4-dioxane), or whether -ane is to be used for saturated hydrocarbons only. It is clear, however, that -ane should *not* be used for any substance not completely saturated. The above changes are not possible in German, since *e* is the sign of the plural (*cf.* rule 3).

15. When nitrogenous heterocycles not having the ending *ine* give basic compounds on progressive hydrogenation, such derivation will be indicated by the successive endings *ine*, *idine*. Examples: pyrrole, pyrroline, pyrrolidine; oxazole, oxazoline.

This rule merely recognizes and extends a well-established practice.

16. The ending *a* is adopted for hetero atoms occurring in a ring. Oxygen will accordingly be indicated by *oxa*, sulfur by *thia*, nitrogen by *aza*, etc. The letter *a* may be elided before a vowel. Examples: thiadiazole, oxadiazole, thiazine, oxazine.

While the universally accepted names of heterocyclic compounds are retained, the names of other heterocyclic compounds are derived from that of the corresponding homocyclic compound by adding to it the names of the hetero atoms ending in *a*. Example: 2,7,9-triazaphenanthrene.



The use of *a* in such prefixes as oxa-, thia- and aza- distinguishes these forms clearly from oxy-, thio-, azo-, etc., which have other meanings. The "a" prefixes may be used either (1) to form such names as *thiadiazole*, or (2) to denote the replacement of a carbon atom or hydrocarbon grouping by a hetero atom or grouping, as stated in the second paragraph of the rule. This latter method is a very useful one, especially in naming bridged heterocyclic compounds, but there are objections to making it the sole method for naming new forms. Among these objections are (1) that in certain cases the hetero atom would be given a different numbering in two tautomeric compounds, thus making it appear that the hetero atom has shifted instead of a hydrogen atom;[6] (2) that in some cases the corresponding homocyclic compounds are not known and that the known heterocyclic compound is more readily named from its own component rings; and (3) that in the case of nitrogen bases the method yields names that do not end in -ine.

The writer therefore sought to have this rule modified so as to make it clear that the use of the "a" nomenclature is permissive only. His impression is that it was the intention of the Committee to so modify the rule at Liége, but the modification does not appear in the final version. The Committee surely cannot have intended to abrogate the well-established practice of forming such names as anthrapyrrole and naphthopyridine, in which the prefix denotes a form which is "fused" with the form whose name follows it. Both practices should be permitted, in the writer's opinion. The older practice can be preserved along with the new if, in accordance with rule 1, a broad interpretation is given to the words, "The names of heterocyclic compounds which are universally adopted will be retained." It is interesting to note that the German version reads: "Wo ein solcher Name fehlt, *kann* der Name," etc., and accordingly makes the use of the "a" nomenclature in such cases permissive only.

IV. Simple Functions

17. Substances of simple function are defined as those containing a function of one kind only, which may be repeated several times in the same molecule.

That is to say, a compound which is an acid, an alcohol or an aldehyde and only that, is defined as a substance of simple function, while one which is at the same time an alcohol and an acid, or an acid and an aldehyde, is said to be a substance of complex function.

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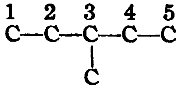
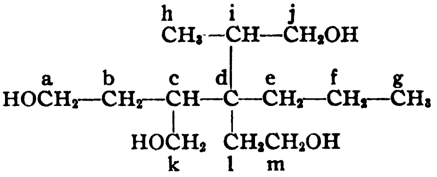
(6) For an example see Patterson, THIS JOURNAL, 50, 3084 (1928).

(7) *Ber.*, 65A, 11-20 (1932).

18. When there is only one functional group, the fundamental chain will be selected so as to contain this group. When there are several functional groups the fundamental chain will be selected so as to contain the maximum number of these groups.

This is an important modification of the Geneva system. The central idea of the latter, so far as aliphatic compounds are concerned, is a fixed carbon skeleton with a fixed numbering, analogous to the fixed scheme for parent cyclic compounds, such as anthracene or quinoline. Hence the longest carbon chain in the molecule and the length and position of the side chains attached to it become of first importance—functional groups such as OH or COOH may come where they will. An example of such a skeleton is  $\overset{1}{\mathrm{C}}-\overset{2}{\mathrm{C}}-\underset{\mathrm{C}}{\overset{3}{\mathrm{C}}}-\overset{4}{\mathrm{C}}-\overset{5}{\mathrm{C}}$ and the saturated hydrocarbon corresponding to it is 3-methylpentane. Suppose carbon atom number 1 and the carbon atom of the side chain in 3-methylpentane to be oxidized to carboxyl groups. According to the Geneva system the original numbering is retained and the compound is called pentanoic-3-methyloic acid. But chemists commonly call this substance ethylsuccinic acid and thereby choose as the fundamental chain the one containing the two carboxyl groups. These groups have a far greater influence upon the properties of the compound than an extra methyl or ethyl group, so it seems natural to treat the compound as a derivative of the corresponding straight-chain diacid rather than as a modified 3-methylpentane. The Committee has recognized this very common principle of nomenclature in rule 18. The functional groups, and not the complete skeleton, are given the place of first importance. By rules 18 and 29 the systematic name of ethylsuccinic acid becomes 2-ethyl-butanedioic acid.

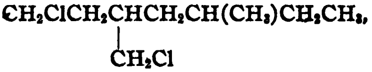
If there are two or more choices for the chain containing the maximum of functional groups, then the principle of rule 6 should be applied (although rule 18 does not so state). That is, the longest chain should be chosen as the fundamental one and if there is still a choice to be made, then the one involving a maximum of substitutions. Example:



$$\begin{array}{ccccccc} & & & \overset{h}{\mathrm{CH_3}}-\overset{i}{\mathrm{CH}}-\overset{j}{\mathrm{CH_2OH}} & & & \\ & & & | & & & \\ \overset{a}{\mathrm{HOCH_2}}- & \overset{b}{\mathrm{CH_2}}- & \overset{c}{\mathrm{CH}}- & \overset{d}{\mathrm{C}}- & \overset{e}{\mathrm{CH_2}}- & \overset{f}{\mathrm{CH_2}}- & \overset{g}{\mathrm{CH_3}} \\ & & | & | & & & \\ & & \underset{k}{\mathrm{HOCH_2}} & \underset{l\ \ \ m}{\mathrm{CH_2CH_2OH}} & & & \end{array}$$

In this compound the maximum of functional groups in any straight chain is two. The longest chain in the molecule is abcdefg = 7, but it contains only one OH group. Those containing two OH groups are: abck = 4, kcdlm = 5, jidlm = 5, abcdij = 6 and abcdlm = 6. The choice therefore lies between the two 6-membered chains. Of these, abcdij has one more substitution than the other and therefore becomes the fundamental chain. The compound accordingly receives the name (numbering j = 1, i = 2, d = 3, c = 4, b = 5 and a = 6): 3-(2-hydroxyethyl)-4-(hydroxymethyl)-2-methyl-3-propyl-1,6-hexanediol.

Should rule 18 be applied to halogen substitution products of the hydrocarbons? At first glance one would infer so, since "halogenide" is listed as a function in rule 52. The real purpose for rule 18, however, in the writer's opinion, is to ensure that all, or as many as possible, of the groups of the principal function (see rule 51) may be expressed in the ending of the name. Rule 18, although it occurs under the heading "Simple Functions" is therefore to be regarded as a complement to rule 51; it should be understood to apply to the principal function (and to it only) when other functions are present. Now, according to rules 19 and 52, halogen functions are to be expressed by prefixes only and there is no utility in applying rule 18 to them *or to any other function when it is expressed as a prefix.* The nitro and nitroso functions are other instances of functions which are expressed as prefixes only. It seems better, and more in accord with present usage, to allow chloro, bromo, nitro, etc., derivatives to be named as derivatives of the longest chain present in the molecule. Example:



$$CH_2ClCH_2\underset{\displaystyle CH_2Cl}{\underset{|}{C}}HCH_2CH(CH_3)CH_2CH_3,$$

1-chloro-3-chloromethyl-5-methylheptane and not 1,4-dichloro-2-(2-methylbutyl)-butane.

19. Halogen derivatives will be designated by the name of the hydrocarbon from which they are derived, preceded by a prefix indicating the nature and number of the halogen atoms.

Examination of text-books shows a prevailing use of such names as ethyl chloride, amyl iodide, hexyl bromide. These compounds are usually, however, of very simple structure. A perusal of the journals will show that the more complex halogen derivatives cannot be conveniently named in this manner and as a matter of fact are nearly always named with the use of prefixes. Rule 19 recommends that prefixes be employed in all cases and we have therefore chloromethane instead of methyl chloride, 1-chlorobutane instead of *n*-butyl chloride, 1,2-dichloroethane instead of ethylene chloride, and so on, although by rule 1 the older names may still be used.

20. Alcohols and phenols will be given the name of the hydrocarbon from which they are derived, followed by the suffix *ol.* In accordance with rule 1 names universally adopted will be retained, as: phenol, cresol, naphthol, etc.

This nomenclature may also be applied to heterocycles. Example: quinolinol.

This is the Geneva nomenclature, with an extension to heterocyclic compounds. Examples: CH_3CH_2OH, ethanol; $CH_3CHOHCH_3$, 2-propanol; cyclohexanol; fluorenol (for hydroxyfluorene); quinolinol (for hydroxyquinoline), etc.

By rule 14, names ending in -ol for substances which are not alcohols or phenols are to be spelled -ole. Similarly, trivial names of alcohols and phenols should end in -ol (as, mannitol instead of mannite, resorcinol instead of resorcin).

21. In naming polyhydric alcohols or phenols, one of the forms *di, tri, tetra,* etc., will be inserted between the name of the parent hydrocarbon and the suffix *ol.*

Examples: CH_2OHCH_2OH, 1,2-ethanediol; $CH_2OHCHOHCH_2OH$, 1,2,3-propanetriol; $C_6H_4(OH)_2$, benzenediol; $C_{10}H_4(OH)_4$, naphthalenetetrol.

22. The name *mercaptan* as a suffix is abandoned; this function will be denoted by the suffix *thiol.*

Examples: CH_3SH, methanethiol; C_6H_5SH, benzenethiol; CH_2SHCH_2SH, 1,2-ethanedithiol.

23. Ethers are considered as hydrocarbons in which one or several hydrogen atoms are replaced by alkoxy groups. However, for symmetrical ethers the present nomenclature may be retained. Examples: $CH_3OC_2H_5$, methoxyethane; CH_3OCH_3, methoxymethane or methyl ether.

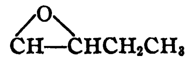
The ether function is treated as a relatively unimportant one, in naming, probably because it is so slightly reactive. Also, like all functions involving a bivalent radical, it causes some difficulties in nomenclature. In this rule the Committee subordinates it to the hydrocarbon and provides that it be expressed in a prefix rather than in the ending of the name. A concession is made to usage in recognizing also the usual names of the simple ethers. In naming by the alkoxy method the larger radical should be chosen for the parent compound. The method is to be extended, presumably, to cyclic compounds. Examples: CH_3OCH_3, methoxymethane or methyl ether; $CH_3OC_2H_5$, methoxyethane; $CH_3OC_4H_3O$, methoxyfuran; $C_6H_5OC_{10}H_7$, phenoxynaphthalene; $CH_3OCH_2CH_2OCH_3$, 1,2-dimethoxyethane.

24. Oxygen linked, in a chain of carbon atoms, to two of these atoms will be denoted by the prefix *epoxy* in all cases where it would be unprofitable to name the substance as a cyclic compound. Examples: ethylene oxide = epoxyethane; epichlorohydrin = 3-chloro-1,2-epoxypropane; tetramethylene oxide = 1,4-epoxybutane.

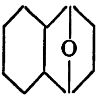
Rule 24 was no doubt given this position because it refers to a special case of the ether function. The prefix *epoxy* is not intended to supplant the regular cyclic names but to be used only where the latter are inconvenient. It will probably find its most common use in cases where a double bond has been oxidized and it is desired to bring out this relationship. Example:

$CH_2{=}CHCH_2CH_3$
1-butene

$CH_2OHCHOHCH_2CH_3$
1,2-butanediol


$\overbrace{CH\text{—}C}^{O}HCH_2CH_3$
1,2-epoxybutane

Another opportunity for its use will be found in bridged compounds; as, 1,4-epoxynaphthalene:



25. Sulfides, disulfides, sulfoxides and sulfones will be named like the ethers, *oxy* being replaced by *thio, dithio, sulfinyl* and *sulfonyl*, respectively. Examples: $CH_3SO_2C_2H_5$, methylsulfonylethane; $CH_3SC_3H_7$, methylthiopropane; $CH_3CH_2CH_2SOCH_2CH_2CH_2CH_3$, 1-(propylsulfinyl)butane.

Further examples: $CH_3SSC_6H_5$, methyldithiobenzene; $C_6H_5SOC_{10}H_7$, phenylsulfinylnaphthalene; $CH_3SO_2C_4H_3O$, methylsulfonylfuran. Presumably the provision about symmetrical compounds in rule 23 applies here also, according to which CH_3SCH_3 could be called methylthiomethane or methyl sulfide; $C_2H_5SOC_2H_5$, ethylsulfinylethane or ethyl sulfoxide, etc.

26. Aldehydes are characterized by the suffix *al* added to the name of the hydrocarbon from which they are derived; thioaldehydes, by the suffix *thial*. Acetals will be named as 1,1-dialkoxyalkanes.

Aliphatic aldehydes and thioaldehydes are named in the above manner in the Geneva system. Examples: CH_3CHO, ethanal; $CHOCHO$, ethanedial; CH_3CH_2CHS, propanethial; $CH_3C(OC_2H_5)_2$, 1,1-diethoxyethane. No provision is made in the rules for aldehydes in which the CHO group is attached directly to a ring (compare rule 49). By analogy with the suffixes -carbonamide, -carbonitrile, etc., the suffix for a substituting CHO group would be *-carbonal*, and C_6H_5CHO, for example, would be named benzenecarbonal (naturally, by rule 1, the common name benzaldehyde would also be recognized). Similarly, $C_5H_3N(CHO)_2$ would be named pyridinedicarbonal.

27. Ketones will receive the ending *one*. Diketones, triketones, thioketones will be designated by the suffixes *dione, trione, thione*.

This is a Geneva rule which has justified itself in practice for aliphatic compounds. Examples: CH_3COCH_3, propanone; CH_3CSCH_3, propanethione; $CH_3COCOCH_3$, 2,3-butanedione. So, also, cyclohexanone, 1,4-cyclohexanedione, etc. The rules make no provision for ketone groups in side chains in the cyclic series (compare rule 49).

28. The name *ketene* is retained.

"Ketene" (or, as spelled by some, "keten") is accordingly recognized as a name for the parent compound $CH_2{=}CO$. It was at one time proposed to call this compound "ethenone" or "ketenone" but the Committee finally decided not to disturb already established usage. Example: $(CH_3)_2C{=}CO$, dimethylketene.

29. For acids the rule of the Geneva nomenclature is retained. However, in cases where the use of that nomenclature would not be convenient the carboxyl group will be considered as a substituting group and the name of the acid will be formed by adding to the name of the hydrocarbon the suffix *carbonique* or *carboxylic*, according to the language.

This rule on the naming of acids is a frank compromise between two conflicting ideas, whose advantages and disadvantages led to much discussion both in the Geneva Congress and in the International Committee. By the Geneva rules aliphatic acids are regarded as derived from hydrocarbons of the same number of carbon atoms (CH_3 being replaced by COOH). The acid name is formed from the hydrocarbon name by adding to it *-oic acid, -dioic acid*, etc. Such names are convenient for simple monoacids and diacids, but become less so as the structure grows more complicated. In the latter case most chemists will probably prefer the "carboxylic" nomenclature. Examples of both systems are given below, with their respective numberings. By rule 1, the familiar names of acids, as butyric, succinic, may also be used.

4 3 2 1 $CH_3CH_2CH_2CO_2H$ butanoic acid	3 2 1 $CH_3CH_2CH_2CO_2H$ 1-propanecarboxylic acid
12 3 4 $HO_2CCH_2CH_2CO_2H$ butanedioic acid	1 2 $HO_2CCH_2CH_2CO_2H$ 1,2-ethanedicarboxylic acid
4 3 2 1 $CH_3CH(CH_3)CH_2CO_2H$ 3-methylbutanoic acid	3 2 1 $CH_3CH(CH_3)CH_2CO_2H$ 2-methyl-1-propanecarboxylic acid
1 2 3 4 5 $CH_3CH_2CH(CO_2H)CH_2CH_3$ pentane-3-methyloic acid	1 2 3 4 5 $CH_3CH_2CH(CO_2H)CH_2CH_3$ 3-pentanecarboxylic acid (or 1-ethyl-1-propanecarboxylic acid)
12 3 4 5 $HO_2CCH_2CH(CO_2H)CH_2CO_2H$ pentanedioic-3-methyloic acid	1 2 3 $HO_2CCH_2CH(CO_2H)CH_2CO_2H$ 1,2,3-propanetricarboxylic acid
4 3 2 1 $CH_2{=}CHCH_2CO_2H$ 3-butenoic acid	3 2 1 $CH_2{=}CHCH_2CO_2H$ 2-propene-1-carboxylic acid (*cf.* rule 64)

In the original Geneva system side chains and double bonds take precedence over the carboxyl groups in determining the numbering. Such numberings are contrary to rule 64 and hence in the examples above they have been revised to give carboxyl low numbers. In most of the carboxylic numberings the figures 1, 2, 3 correspond to the familiar α, β, γ. The Geneva rules refer to aliphatic acids only, hence where the carboxyl group is directly attached to a ring the "carboxylic" nomenclature is to be followed. Example: C_6H_5COOH, benzene-carboxylic acid (or benzoic acid).

It will be noted that in the Geneva names of acids a side chain containing a carboxyl group is expressed as "methyloic" (—COOH), "ethyloic" (—CH_2COOH), etc. (see examples 4 and 5, above). In the "carboxylic" nomenclature, presumably any carboxyl group which is not attached to the fundamental chain is to be expressed by the prefix "carboxy;" as, $HOOCCH_2C(CH_2COOH)(COOH)CH_2COOH$, pentanedioic-3-methyloic-3-ethyloic acid (Geneva name) or 2-(carboxymethyl)-1,2,3-propanetricarboxylic acid ("carboxylic" name).

30. Acids in which an atom of sulfur replaces an atom of oxygen will be named according to the Geneva nomenclature. Example: ethanethioic, -thiolic, -thionic, -thionothiolic. If the carboxyl is considered as a substituent the compounds will be named *carbothioic* acids. The suffix *carbothiolic* will be used if it is certain that the oxygen of the OH group is replaced by sulfur; the suffix *carbothionic* if it is the oxygen of the CO group; the suffix *carbodithioic* will be used if both oxygen atoms are replaced.

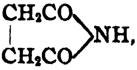
Examples of the two systems of names: CH_3COSH or CH_3CSOH (either one), ethanethioic acid, methanecarbothioic acid; CH_3COSH, ethanethiolic acid, methanecarbothiolic acid; CH_3CSOH, ethanethionic acid, methanecarbothionic acid; CH_3-CSSH, ethanethionothiolic acid, methanecarbodithioic acid.

31. The existing conventions will be retained for salts and esters.

Examples: Sodium butanoate or sodium salt of butanoic acid; diethyl 1,2-ethanedicarboxylate or diethyl ester of 1,2-ethanedicarboxylic acid; sodium acetate; methyl succinate.

32. Acid anhydrides will retain their present mode of designation according to the names of the corresponding acids. For names formed in accordance with the Geneva nomenclature, the amides, amidoximes, amidines, imides and nitriles will be named like the acids by adding to the name of the corresponding hydrocarbon the endings *amide*, *amidine*, *amidoxime*, *imide* and *nitrile*, respectively, while the halides will be named by combining *chloride*, etc., with the name of the radical. Examples: C_3H_7COCl, butanoyl chloride; $C_3H_7CONH_2$, butanamide; etc.

If the carboxyl is considered as a substituent the endings *carbonamide*, *carbonamidine*, *carbonamidoxime*, *carbonimide*, *carbonitrile* will be used. Examples: C_3H_7COCl, propanecarbonyl chloride; $C_3H_7CONH_2$, propanecarbonamide; etc.

Further examples: $(CH_3CO)_2O$, ethanoic anhydride or methanecarboxylic anhydride (also acetic anhydride); CH_3CONH_2, ethanamide or methanecarbonamide; $CH_3C({=}NH)NH_2$, ethanamidine or methanecarbonamidine; $CH_3C({=}NOH)NH_2$, ethanamidoxime or methanecarbonamidoxime;  $\left.\begin{matrix}CH_2CO\\ |\\ CH_2CO\end{matrix}\right\rangle NH$, butamide or 1,2-ethanedicarbonimide; CH_3CN, ethanenitrile or methanecarbonitrile; CH_3COCl, ethanoyl chloride or methanecarbonyl chloride (*cf.* rule 58).

English-speaking chemists may, if they desire, use *-carboxamide* or *-carboxylamide* instead of -carbonamide, and so on (*cf.* rules 3 and 29) but it is well not to introduce any more such language differences than are necessary.

33. The ending *ine* is reserved exclusively for nitrogenous bases. The present nomenclature of monoamines is retained. For polyamines, the name of the hydrocarbon will be followed by the suffixes *diamine*, *triamine*, etc.

For aliphatic compounds containing quinquevalent nitrogen the ending *ine* will be changed to *onium*. For cyclic substances containing quinquevalent nitrogen in the ring the ending *ine* will be changed to *inium;* for those with the ending *ole*, this will be changed to *olium*. Examples: pyridine, pyridinium; imidazole, imidazolium.

In accordance with the first sentence of this rule the spelling of names of non-bases ending in -ine should be changed; thus glycerine becomes glycerol, dextrine becomes dextrin, propine becomes propyne (see rule 9). Examples of names of amines: CH_3NH_2, methylamine; $(CH_3)_2NH$, dimethylamine; $(CH_3)_3N$, trimethylamine; $H_2NCH_2CH_2NH_2$, 1,2-ethanediamine; $C_6H_4(NH_2)_2$, benzenediamine.

34. The nomenclature of the derivatives of phosphorus, arsenic, antimony and bismuth, being very complicated, will be considered later.

Usage in this field needs systematizing but the Committee could not agree upon a plan. The scheme proposed by the American Committee for the acids of phosphorus, arsenic and antimony was as follows (with "phosph" and "stib" corresponding to "ars"):

Formula	Prefix	Suffix
$RR'AsOH$	Arsinoso	Arsinous
$RAs(OH)_2$	Arsonoso	Arsonous
$RR'AsO.OH$	Arsino	Arsinic
$RAsO(OH)_2$	Arsono	Arsonic

35. Compounds derived from hydroxylamine by replacement of the hydrogen of the hydroxyl will be regarded as alkoxy derivatives; those in which an atom of hydrogen of the NH_2 group is replaced, as alkylhydroxylamines. Oximes will be named by adding the suffix *oxime* to the name of the corresponding aldehyde, ketone or quinone. Examples: $C_2H_5ONH_2$, ethoxyamine; C_2H_5NHOH, ethylhydroxylamine.

Further examples: $CH_3CH_2CH{=}NOH$, propanal oxime; $CH_3C({=}NOH)CH_3$, propanone oxime.

36. The generic term *urea* is retained; it will be used as a suffix for the alkyl and acyl derivatives of urea. Examples: butylurea, $C_4H_9NHCONH_2$; butyrylurea, $C_3H_7CONHCONH_2$. The bivalent radical —NHCONH— will be named *ureylene*.

Butyrylurea may also be called butanoylurea or propanecarbonylurea. Nothing is said about polysubstituted ureas.

37. The generic name *guanidine* is retained.

38. The name *carbylamine* is retained.

In earlier drafts the terms *isonitrile* and *isocarbonitrile* were favored and *carbylamine* was rejected. The latter was apparently restored at the instance of Professor Grignard, who believed there should be more of a distinction from nitriles than the prefix "iso" gives. No examples are given but the form favored by custom seems to be: ethylcarbylamine, C_2H_5NC. No objection seems to have been raised to *isocyanide*, a term also in use for these compounds (as, ethyl isocyanide).

39. Isocyanic and isothiocyanic esters (RNCO, RNCS) will be named *isocyanates* and *isothiocyanates*.

Examples: ethyl isocyanate, C_2H_5NCO; ethyl isothiocyanate, C_2H_5NCS.

40. The name *cyanate* is reserved for true esters which on saponification yield cyanic acid or its hydration products. The name *sulfocyanate* will be replaced by *thiocyanate*.

This is Geneva rule 44 with slightly altered wording. Examples: C_2H_5CNO, ethyl cyanate; C_2H_5CNS, ethyl thiocyanate.

41. Nitro derivatives: no change in the present nomenclature.

That is, the group NO_2 is always indicated by the prefix *nitro*, never by a suffix. Nitroso compounds are treated similarly (see rule 52). Examples: nitrosobenzene, 2,4,6-trinitrophenol.

42. Azo derivatives: the forms *azo*, *azoxy* are retained.

This rule is rather non-committal, as it does not state how the azo and azoxy names are to be formed. By rule 1 familiar terms like azobenzene, $C_6H_5N_2C_6H_5$, would be retained. The Geneva name for this substance is benzeneazobenzene. In treating the group $C_6H_5N_2$ as a substituent the Committee does not indicate whether it should be called "benzeneazo" or "phenylazo" (the latter would seem to accord best with rules 23 and 25). The same considerations apply to azoxy compounds. Hydrazo compounds are treated as hydrazine derivatives (rule 44).

43. (a) Diazonium compounds, RN_2X, are named by addition of the suffix *diazonium* to the name of the parent substance (benzenediazonium chloride).

(b) Compounds having the same empirical formula but containing trivalent nitrogen will be named by replacing diazonium with *diazo* (benzenediazohydroxide).

(c) Substances of the type RN_2OM will be named *diazoates*.

(d) Compounds in which the two nitrogen atoms are united to a single carbon atom will be designated by the prefix *diazo* (diazomethane, diazoacetic acid).

(e) The term *diazoamino* is retained; however, these compounds may also be regarded as derivatives of triazene.

(f) Derivatives of the substances $H_2NNHNHNH_2$; $NH{=}NNHNH_2$; $NH{=}NNHN{=}NH$ will be named *tetrazanes*, *tetrazenes*, *pentazdienes*, etc.

Examples: (a) $C_6H_5N(\equiv N)Cl$, benzenediazonium chloride; (b) $C_6H_5N{=}NOH$, benzenediazohydroxide; (c) $C_6H_5N{=}NONa$, sodium benzenediazoate; (d) N_2CH_2, diazomethane; N_2CH_2COOH, diazoacetic acid, diazoethanoic acid or diazomethanecarboxylic acid; (e) $C_6H_5N{=}NNHC_6H_5$, diazoaminobenzene or 1,3-diphenyltriazene; (f) $C_6H_5NHNHNHNHC_6H_5$, 1,4-diphenyltetrazane; $C_6H_5N{=}NNHNH_2$, 1-phenyl-1-tetrazene. (The numberings are the writer's.)

44. Hydrazines are designated by the name of the alkyl radicals from

which they are derived, followed by the suffix *hydrazine*. In cases where the amino group of carbonamides is replaced by the hydrazino group, the suffix *hydrazide* will be used. Hydrazo derivatives are regarded as derivatives of hydrazine. Examples: CH_3NHNH_2, methylhydrazine; $C_2H_5NHNHC_3H_7$, 1-ethyl-2-propylhydrazine; $C_3H_7CONHNH_2$, butyrohydrazide or propanecarbohydrazide.

The name for $C_3H_7CONHNH_2$ which corresponds to the Geneva name for the acid would probably be butanohydrazide, although neither the Geneva rules nor the present rules say so explicitly. The cases of *poly*substituted hydrazines in which one or more substituents are acid radicals are not covered by the rule. If there is more than one acyl substituent the compound is possibly best named by analogy with rule 36; example: $CH_3CONHNHCOCH_3$, 1,2-diacetylhydrazine, 1,2-diethanoylhydrazine, or 1,2-bis(methanecarbonyl)hydrazine. If there is only one acyl substituent it might be named by analogy with rule 36 (example, $CH_3CONHNHC_2H_5$, 1-acetyl-2-ethylhydrazine) or as a substituted hydrazide (in the latter case, however, the two nitrogen atoms would have to be distinguished in some way). By rule 1, $C_6H_5NHNHC_6H_5$ may still be called hydrazobenzene as well as 1,2-diphenylhydrazine.

45. Hydrazones and semicarbazones are named like the oximes. The term *osazone* is retained.

Examples: $CH_3CH{=}NNHC_6H_5$, ethanal (or acetaldehyde) phenylhydrazone; $(CH_3)_2C{=}NNHCONH_2$, propanone (or acetone) semicarbazone.

46. The name *quinone* is retained.

Examples: *p*-benzoquinone or *p*-quinone, 1,2-naphthoquinone or 1,2-naphthaquinone, phenanthrenequinone or phenanthraquinone.

47. Sulfonic and sulfinic acids will be designated by adding the suffixes *sulfonic* and *sulfinic* to the name of the hydrocarbon.

The analogous acids of selenium and tellurium will bear the names *alkaneselenonic* and *-seleninic* acids; *alkanetelluronic* and *-tellurinic* acids.

Examples: $C_2H_5SO_3H$, ethanesulfonic acid; $C_{10}H_6(SO_2H)_2$, naphthalenedisulfinic acid; CH_3SeO_3H, methaneselenonic acid; $C_6H_5TeO_2H$, benzenetellurinic acid. The radicals of these acids would presumably be named by replacing "ic acid" by *yl;* as CH_3SO_2Cl, methanesulfonyl chloride (but meth*yl*sulfonylethane; *cf.* rule 25). The amides would presumably be named by replacing "ic acid" by *amide* (as, $C_6H_5SO_2NH_2$, benzenesulfonamide), etc. *Cf.* rule 32.

48. Organometallic compounds will be designated by the names of the organic radicals united to the metal which they contain, followed by the name of the metal. Examples: dimethylzinc, tetraethyllead, methylmagnesium chloride.

However, if the metal is united in a complex manner it may be considered as a substituent. Example: $ClHgC_6H_4CO_2H$, chloromercuribenzoic acid.

The rule gives no examples for compounds in which a second metal is present, but the name "methylmagnesium chloride" suggests the principle that organic radicals may be denoted by prefixes attached to one part of a binary inorganic name. Hence, we might risk as a further example: $(C_6H_5)_3SnNa$, sodium triphenylstannide.

49. The nomenclature of cyclic derivatives having side chains will be considered later.

An earlier draft attempted to treat, in two paragraphs, cyclic derivatives with one and with more than one side chain but it became evident that much further study was needed.

50. If it is necessary to avoid ambiguity, the names of complex radicals will be placed in parentheses. Examples: (dimethylphenyl)amine = $(CH_3)_2C_6H_3NH_2$; dimethylphenylamine = $C_6H_5N(CH_3)_2$.

V. Complex Functions

51. For compounds of complex function, that is to say, for compounds possessing different functions, only one kind of function (the principal function) will be expressed by the ending of the name. The other functions will be designated by appropriate prefixes.

This is a definite departure from the Geneva system, since the latter permits functional suffixes to pile up in the names of mixed compounds (as, pentanaloloic acid). The Committee's decision is in accord with usage. The writer, in a study of the names of compounds of complex function in journal and book literature,[8] found 2557 instances in which only one of the functions present was expressed in the ending, as contrasted with 251 names in which two or more were so expressed. In certain cases it seems unavoidable that more than one function be expressed in the ending; as, butenyne, butenol, quinolinesulfonic (*-ene*, *-yne* and *-ine* have no corresponding prefixes).

52. The following prefixes and suffixes will be used for designating the functions.

Function	Prefix	Suffix
Acid and derivatives	carboxy	carboxylic, carbonyl, carbonamide, etc., or oic, oyl, etc.
Alcohol	hydroxy	ol
Aldehyde	oxo, aldo (for aldehyde O) or formyl (for CHO)	al
Amine	amino	amine
Azo derivative	azo	....
Azoxy derivative	azoxy	....
Carbonitrile (nitrile)	cyano	carbonitrile or nitrile
Double bond	....	ene
Ether	alkoxy	....
Ethylene oxide, etc.	epoxy	....
Halide	halogeno [halo]	....
Hydrazine	hydrazino	hydrazine
Ketone	oxo or keto	one
Mercaptan	mercapto	thiol
Nitro derivative	nitro	....

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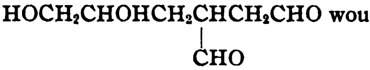
[8] Patterson, *Rec. trav. chim.*, **48**, 1016 (1929).

Function	Prefix	Suffix
Nitroso derivative	nitroso	....
Quinquevalent nitrogen	....	onium, inium [olium]
Sulfide	alkylthio	....
Sulfinic derivative	sulfino	sulfinic
Sulfone	sulfonyl	....
Sulfonic derivative	sulfo	sulfonic
Sulfoxide	sulfinyl	....
Triple bond	....	yne
Urea	ureido	urea

The order of functions in the French version is alphabetic and has no significance. The entries have been transposed in the translation in order to give an alphabetic arrangement in English also. The Committee intended at one time to establish an *order of precedence of functions* (to determine which should be the principal function in a compound containing two or more different functions), but later gave up the idea. The study of the writer already referred to under rule 51 indicates that it will be difficult to construct any order that will agree closely with general usage.[9]

As to the choice of the fundamental chain in compounds of complex function, the writer's opinion is, that by analogy with rule 18 (which treats of simple functions) the fundamental chain should be so chosen as to contain as many of the principal functional groups as possible, even if this is not the longest chain in the molecule or the chain which contains the most functional groups of all kinds. A correct name for the compound  $HOCH_2CHOHCH_2\underset{\displaystyle CHO}{\underset{|}{C}}HCH_2CHO$ would therefore be 2-(2,3-dihydroxypropyl)butanedial, rather than 3-formyl-5,6-dihydroxyhexanal. This is in accord with common usage, which would certainly regard the compound as a derivative of succinaldehyde.

53. The names of derivatives of fundamental heterocyclic substances will be formed according to the preceding rules.

Example: Hydroxyquinolinecarbonamide, not quinolinolcarbonamide.

VI. Radicals

54. Univalent radicals derived from saturated aliphatic hydrocarbons by removal of one atom of hydrogen will be named by replacing the ending *ane* of the hydrocarbon by the ending *yl*.

Examples: methyl, ethyl, pentyl (or amyl), etc. Since isopropylidene is recognized (rule 56) it was no doubt the intention of the Committee to recognize isopropyl similarly.

55. The names of univalent radicals derived from unsaturated aliphatic hydrocarbons will have the endings *enyl, ynyl, dienyl,* etc., the positions of the double or triple bonds being indicated by numerals or letters where necessary

Examples: $CH_2{=}CH{-}$, ethenyl (or vinyl); $CH{\equiv}C{-}$, ethynyl; $CH_3{-}CH{=}CH{-}CH_2{-}$, 2-butenyl; $CH_2{=}CH{-}CH{=}CH{-}$, 1,3-butadienyl.

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[9] For the order used in the *Chemical Abstracts* indexes, see Patterson and Curran, THIS JOURNAL, 39, 1624 (1917).

56. Bivalent or trivalent radicals derived from saturated hydrocarbons by removal of 2 or 3 hydrogen atoms from the same carbon atom will be named by replacing the ending *ane* of the hydrocarbon by the endings *ylidene* or *ylidyne*. For radicals derived from unsaturated hydrocarbons, these endings will be added to the name of the hydrocarbon. The names isopropylidene and methylene are retained.

Examples: $CH_2<$, methylene; $CH_3CH<$, ethylidene; $CH_3CH_2CH<$, propylidene; $(CH_3)_2C<$, (1-methylethylidene) or isopropylidene; $CH_3C\equiv$, ethylidyne; $CH_2{=}CH{-}CH_2CH<$, 3-butenylidene. In the last example the number must be changed from 1 (in the name of the hydrocarbon, 1-butene) to 3 in order to indicate the position of the double bond correctly. The new ending *ylidyne*, formed by analogy with "ylidene," should prove useful.

57. The names of bivalent radicals derived from aliphatic hydrocarbons by removal of a hydrogen atom from each of the two terminal carbon atoms of the chain will be ethylene, trimethylene, tetramethylene, etc.

Only saturated radicals are provided for: $-CH_2CH_2-$, ethylene; $-CH_2CH_2CH_2-$, trimethylene, etc. (In an earlier draft the ending *ylene* was employed, thus: $-CH_2CH_2CH_2CH_2-$, butylene; $-CH_2CH{=}CHCH_2-$, 2-butenylene)

58. Radicals derived from acids by removal of OH will be named by changing the ending carboxylic to *carbonyl* or, if the Geneva nomenclature is used, oic to *oyl*.

Examples: CH_3CO, ethanoyl or methanecarbonyl (or acetyl).

59. Univalent radicals derived from aromatic hydrocarbons by removal of a hydrogen atom from the ring will in principle be named by changing the ending *ene* to *yl*. However, the radicals C_6H_5 and $C_6H_5CH_2$ will continue provisionally to be named phenyl and benzyl, respectively. Moreover, certain abbreviations sanctioned by usage are authorized, as *naphthyl* instead of *naphthalyl*.

Examples: $CH_3C_6H_4-$, tolyl (instead of toluyl), anthryl (instead of anthracyl), phenanthryl, fluoryl.

60. Univalent radicals derived from heterocyclic compounds by removal of hydrogen from the ring will be named by changing their endings to *yl*. In cases where this would give rise to ambiguity, merely the final *e* will be changed to *yl*. Examples: pyridine, pyridyl; indole, indolyl; pyrroline, pyrrolinyl; triazole, triazolyl; triazine, triazinyl.

In this rule the Committee recognizes such accepted short names as pyridyl, quinolyl and furyl but at the same time recommends the longer forms where confusion could arise; thus, indolyl (instead of indyl, which might suggest indene), pyrrolinyl (instead of pyrrolyl, which might suggest pyrrole), triazolyl (instead of triazyl, which might suggest triazine).

61. Radicals formed by removal of a hydrogen atom from a side chain of a cyclic compound will be regarded as substituted aliphatic radicals.

Examples: $C_6H_5CH_2CH_2-$, (2-phenylethyl); $C_6H_5CH{=}CHCH_2-$, (3-phenyl-2-propenyl).

62. In general, special names will not be given to multivalent radicals derived from cyclic compounds by removal of several hydrogen atoms from the ring. In this case prefixes or suffixes will be used. Examples: triaminobenzene or benzenetriamine; dihydroxypyrrole or pyrrolediol.

Comparison with rules 21, 33 and 51 will show that of the names given as examples, "benzenetriamine" and "pyrrolediol" are the ones ordinarily to be preferred (according to the rule of expressing the principal function in the ending of the name where there is a suffix denoting it.)

63. The order in which prefixes or radicals are stated (alphabetic order or conventional order) remains optional.

See the comments on rule 7. There is no generally accepted "conventional order" for all prefixes

VII. Numbering

64. In aliphatic compounds the carbon atoms of the fundamental chain will be numbered from one end to the other with the use of arabic numerals. In case of ambiguity the lowest numbers will be given (1) to the principal function, (2) to double bonds, (3) to triple bonds, (4) to atoms or radicals designated by prefixes. The expression "lowest numbers" signifies those that include the lowest individual number or numbers. Thus, 1,3,5 is lower than 2,4,6; 1,5,5 lower than 2,6,6; 1,2,5 lower than 1,4,5; 1,1,3,4 lower than 1,2,2,4.

Examples: $CH_2{=}CHCH_2CH_3$, 1-butene (not 3-butene); $CH_2{=}CHC{\equiv}CH$, 1-propen-3-yne (not 3-propen-1-yne); $CH_2{=}CH{-}CH_2OH$, 3-propen-1-ol (not 1-propen-3-ol; the name allyl alcohol may also be used); $CHCl_2CH_2CH{=}CH_2$, 4,4-dichloro-1-butene.

The last example illustrates a difficulty of interpretation which might arise, it might be thought that, the numbers 1,1,3 being lower than 1,4,4, the compound should be named 1,1-dichloro-3-butene This, however, was apparently not the intention of the Committee, for 1-butene is the parent compound. The British version makes this interpretation clearer by translating the French "En cas d'ambiguité" rather freely as "To avoid ambiguity."

The principle of "low numbers" also applies to cyclic compounds, with due regard to their different structure (*e. g* , bridges and hetero atoms are usually given preferred positions). Examples: 1,3-cyclohexadiene; 3-cyclohexen-1-one or simply 3-cyclohexenone; 4,4-dichlorocyclohexene.

Position of Numbers.—Where shall position numbers be placed, *before* or *after* the parts of the name to which they refer? Usage varies; some chemists place them before, some place them after, some use a combination. The Committee has left full latitude on this point. The examples in the French version usually show the numbers placed after; the examples in these comments follow the practice of *Chemical Abstracts* in being placed before. Each method has certain advantages. In Beilstein numbers placed after are in parentheses, those placed before are not, *e. g.*, "2-methyl-butanol-(4)."

65. Positions in a side chain will be designated by numerals or letters, starting from the point of attachment. The numerals or letters will be in parentheses with the name of the chain.

Examples: $(CH_3)_2CH{-}$, (1-methylethyl) or isopropyl; $CH_3CHClCH_2{-}$, (2-chloropropyl). The rule equally permits Greek letters, ordinary letters, primed numbers (1′, 2′), numbers with indices (4^1, 4^2) or other designations. Although the original Geneva nomenclature prescribed numbers with indices for side chains they have not been generally used and the present rules do not mention them. Plain numbers or letters usually suffice. The writer prefers to reserve primed numbers for special cases (as for doubled molecules, or for numbering the branched position in isopropyl).

66. In case of ambiguity in the numbering of atoms or radicals designated by prefixes, the order will be that chosen for the prefixes before the name of the fundamental compound or side chain of which they are substituents.

Example: $CH_2BrCH_2CH_2Cl$, 1-bromo-3-chloropropane (alphabetic order), or 1-chloro-3-bromopropane (order of increasing radical weight). The purpose of the rule is to decide which prefixes shall have which numbers, when the set of numbers (in the above example 1,3) for the prefixes has been determined.

67. The prefixes, *di*, *tri*, *tetra*, etc., will be used before simple expressions (for example, diethylbutanetriol) and the prefixes *bis*, *tris*, *tetrakis*, etc., before complex expressions. Examples: bis(methylamino)propane: $CH_3NH(CH_2)_3NHCH_3$; bis(dimethylamino)ethane, $(CH_3)_2NCH_2CH_2N(CH_3)_2$. The prefix *bi* will be used only to denote the doubling of a radical or compound; for example, biphenyl.

Additional example of the use of *bi:* *p*-$(C_6H_4CO_2H)_2$, 4,4′-bibenzoic acid or biphenyl-4,4′-dicarboxylic acid.

68. A catalog of cyclic systems, with their numberings according both to the existing system and to that of Mr. Patterson, is in preparation under the auspices of the National Research Council of the United States and of the American Chemical Society.

Work on this project is now in abeyance pending better financial conditions for publication.

In order to avoid all confusion the Commission recommends placing a scheme of numbering at the head of each article.

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Diffusion as an Aid in the Analysis of Gaseous Paraffin Hydrocarbon Mixtures

BY ROBERT A. BAXTER AND LELAND J. BECKHAM

The purpose of the present investigation is the development of a supplementary procedure to be used in conjunction with the usual combustion analysis on paraffin hydrocarbon gases in order to increase the information attainable. It is a well-known fact that lighter gases will diffuse more rapidly than heavy ones. Thus if a mixture of several gases be allowed to undergo partial diffusion, the residue remaining after part of the gases have diffused away will have a composition which is richer in the heavier constituents. This change in composition can be calculated by means of the kinetic theory.

The present paper describes an apparatus suitable for this determination, together with charts for its application to ordinary analytical practice.

The apparatus (Fig. 3), later described in detail, is operated as follows. The hydrocarbon mixture is introduced into the apparatus, the orifice opened and the gases allowed to diffuse into the air for a certain period of time; the stopper is then replaced, and a sample withdrawn for the usual combustion analysis. From the results of this combustion analysis and from one on the original mixture before diffusion, and by the use of proper equations or charts, considerably more information concerning the nature of the gas sample can be obtained, as is described in this paper.

In the calculation of the composition of gaseous paraffin hydrocarbon mixtures from the results of combustion and absorption data, assumptions are usually made as to the "two most prevalent hydrocarbons" and the analysis is reported in terms of the quantity of these in the mixture.[1] This practice has led to much confusion, particularly when a natural gas is reported as a mixture of ethane and propane before stripping gasoline out of it, and as another mixture of these same two gases after the stripping. The heating value, the air required for combustion, the theoretical flame temperature and the composition of the stack gases resulting from the combustion of any such mixture can be calculated from the analysis reported in this manner. The same results could be obtained from the calculation to any other assumed mixture of paraffin hydrocarbon gases, one of which is lighter, and the other one heavier than the average of the gases actually present. Although several measurable quantities result from the combustion of the gas and the subsequent absorption of the carbon dioxide which is formed, there are only two independent equations, and

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(1) "Methods of the Chemists of the U. S. Steel Co. for the Sampling and Analysis of Gases," Carnegie Steel Co., Pittsburgh, 1927, p. 88. Also see Burrell, Seibert and Jones, *Bur. Mines Bull.*, 197, 96 (1926).

consequently only two hydrocarbons can be calculated. Earnshaw[2] developed the equations by means of which the total volume of paraffin hydrocarbons and the average number of carbon atoms per paraffin molecule may be calculated. Similar equations for various combustible gases were set up by de Voldere and de Smet[3] and condensed by Anderson.[4] A further correlation of these equations was made by Baxter.[5] The evidence in these references is very conclusive as to the superiority of reporting these analyses in terms of the amount of paraffin hydrocarbons of a stated average number of carbon atoms per molecule.

The difference in the diffusion characteristics of gases will produce a measurable difference in the value of n (the average number of carbon atoms per molecule of hydrocarbons in the gas) determined before and after diffusion. From the value of Δn (the increase in n which results from the greater rate of diffusion of the smaller molecules) and the value of n in the original mixture, a new equation is obtained by which the calculation may be extended to three hydrocarbons.

However, the use of this equation for the calculation of three component mixtures requires considerable time and effort for solution; therefore, diagrams of the relationship between n and Δn have been prepared for the two ternary mixtures: methane–ethane–propane (Fig. 1) and methane–ethane–butane (Fig. 2). It is obvious that the sides of these diagrams give the five binary relationships.

If a set of charts is determined for any given apparatus these charts can be used completely in place of numerical calculation and the application of the method is extremely simple and rapid. There are three distinct methods whereby any one wishing to use this procedure could obtain charts for an apparatus which he might construct.

1. The charts might be constructed from the fundamental equations given later in the paper. (The charts shown in this paper were obtained in this manner.)

2. One could so choose the length of time of the run that the same total amount of diffusion would take place as in the apparatus which we used. Then the charts in this paper would be applicable. This could be easily calibrated by determining the proper time so that 80% of a sample of pure methane would diffuse out, as our charts were constructed for this amount of diffusion.

3. A sufficient number of experimental determinations upon known mixtures could be run so that the charts could be plotted entirely from experimental data without resorting to the kinetic equations.

The value of n is obtained by the equation: $n = 3y/(2x - y)$, in which

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(2) Earnshaw, *J. Franklin Inst.*, **146**, 161–176 (1898).

(3) De Voldere and de Smet, *Z. anal. Chem.*, **49**, 661–688 (1910).

(4) R. P. Anderson, see Dennis and Nichols, "Gas Analysis," The Macmillan Co., New York, 1929, Chapt. XII.

(5) Robert A. Baxter, *Color. School Mines Mag.*, **20**, No. 1, 13–16 (1930).

x is volume contraction resulting from combustion and y is volume of carbon dioxide formed by combustion.

For purposes of illustration we will confine our attention to mixtures in which the average value of n as obtained from combustion analysis is 1.60.

The ordinary method of reporting this gas would be as methane and ethane in the ratio of four to six parts by volume in the combustible hydrocarbon mixture. If this happens to be 50% of the original gas sample, the analysis will usually be given as 20% methane and 30% ethane. As pointed out by one of us in an earlier paper to which reference was made above, better information can be obtained by reporting this mixture as 50% total paraffin hydrocarbons of an average value of n = 1.60. The volume of the total paraffin in the sample burned is obtained by the equation: $V = (2x - y)/3$. x and y have the meanings given above. This avoids any unwarranted assumptions.

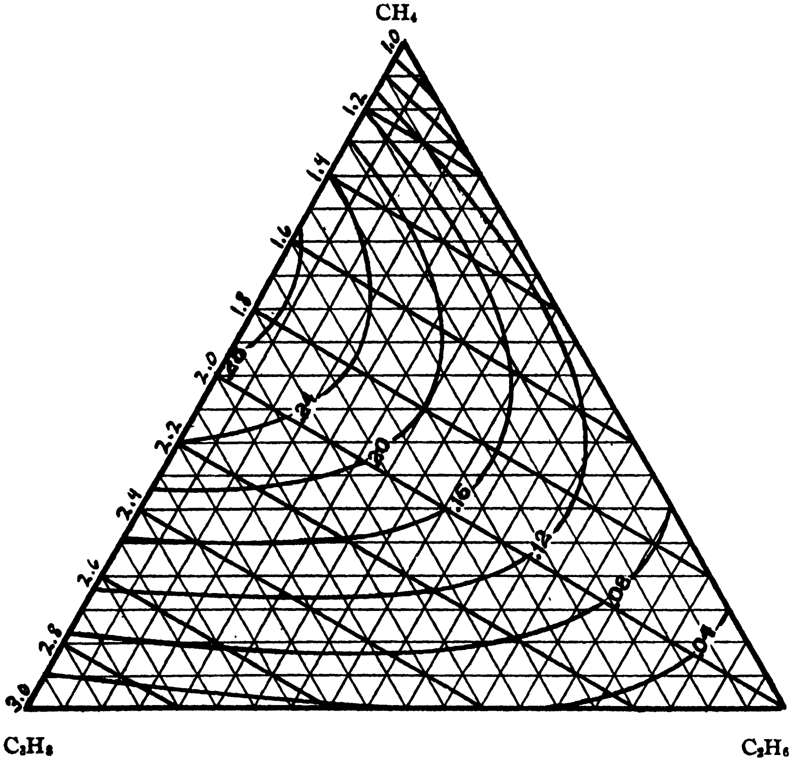

Fig. 1.—Methane–ethane–propane diagram: curved lines are values of Δn.

A glance at the chart or a brief calculation will indicate that one might assume 70% methane and 30% propane, 80% methane and 20% butane, or some corresponding higher ratio of methane to pentane or other hydrocarbons instead of the assumed value of 40% methane and 60% ethane.

In addition, the mixture might be one of methane with two or more higher hydrocarbons. There is just one point which is clear, namely, that in a mixture of paraffin hydrocarbons in which $n = 1.60$, the methane is not less than 40%.

Two gaseous mixtures will be considered. Each has $n = 1.60$. One gives $\Delta n = 0.12$ while the other gives $\Delta n = 0.36$. The intersection of the $\Delta n = 0.12$ curve with the line $n = 1.60$ will first be considered. If the system present is methane–ethane–propane, the propane will be 4% of the entire mixture. If the system present is methane–ethane–butane, the butane will be 2% of the entire mixture. Since still less of any higher paraffin hydrocarbon will be required to have the same effect as the 4% of propane or the 2% of butane, the limits of not less than 96% total methane and ethane mixture, not more than 2% butane, and less than 2% of any higher hydrocarbons are definitely established. The mixture which gives $\Delta n = 0.36$ will now be considered. Since this value is greater than any which appear on the chart for the system methane–ethane–propane, the one first dependable conclusion is that there must be some butane or higher hydrocarbon present. The intersection of the two appropriate

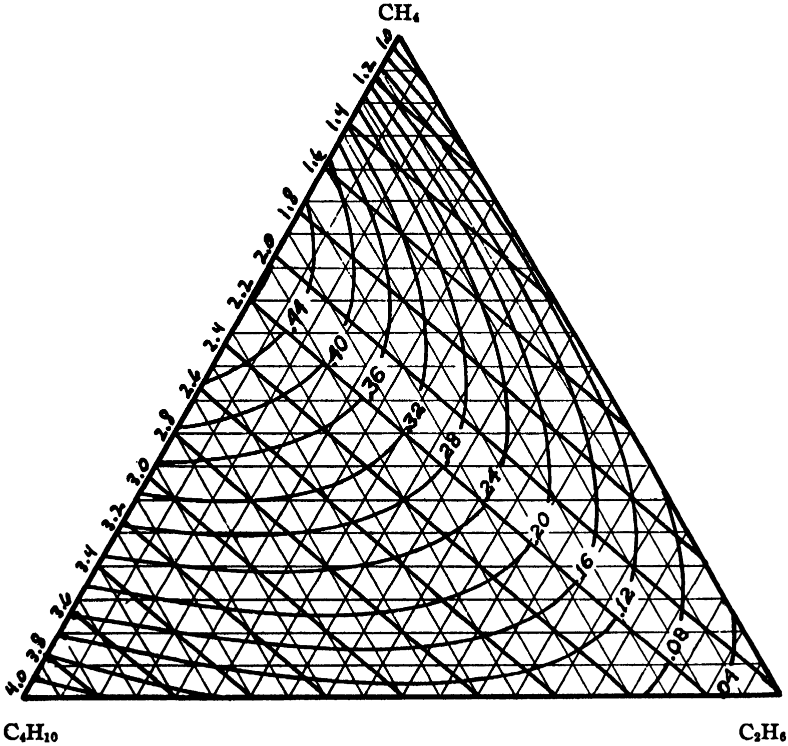

Fig. 2.—Methane–ethane–butane diagram: curved lines are values of Δn.

curves on the methane–ethane–butane diagram indicates that if the system actually happens to consist of these three constituents, the butane must be 17% of the mixture. This is the maximum limit for the butane or heavier hydrocarbons. In case higher ones are present, their amount will be relatively less and the fraction of lighter hydrocarbons relatively more. The minimum amount of methane and ethane cannot be read directly from the methane–ethane–propane diagram as in the former case for the value of Δn does not fall on the chart. However, the minimum can be obtained in this case from a chart constructed for methane–propane–butane. We have constructed only the two charts shown. Similar charts could be constructed for any three assumed hydrocarbons (including hydrogen as a paraffin hydrocarbon in which $n = 0.00$).

The triangular diagrams indicate very definitely the difference between the two gases which would be reported as identical by the conventional method. The gas with $\Delta n = 0.12$ is sufficiently evaluated for most purposes by the diffusion method. The necessity for further work in order to get an accurate evaluation of the one in which $\Delta n = 0.36$ is shown. In general, when the value of Δn is small the analysis as obtained by the combination of diffusion with the combustion and absorption procedures will meet the ordinary analytical requirements, but when the value of Δn is large the presence of higher hydrocarbons is definitely shown. In the latter case the nature of the constituents as well as their concentration is obscure. When Δn is large some type of low-temperature fractional distillation device[6] would probably be the most satisfactory for the separation and identification of the higher boiling constituents. However, this equipment is expensive and more or less complicated, and it requires liquid air or similar material for cooling.

The diffusion method will minimize guessing in the analysis of gaseous mixtures, will itself give sufficient results in many instances, and in the remainder it will give definite indications as to the necessity for using the more complex and expensive methods.

Experimental

Preparation of Materials.—The hydrocarbons used, methane, ethane, propane and butane, were prepared from the corresponding halides by means of the Grignard reaction. The gases were washed with concentrated sulfuric acid and stored over water.

Combustion Analyses.—The combustion and absorption analyses were performed with the laboratory apparatus of the U. S. Steel Corporation[7] using mercury as the confining agent. All samples of gas were analyzed two to eight times, and the average of these values was recorded as the true composition of the gas. The average variation from the mean on the values of n obtained from calculation from the observed data was 0.015.

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(6) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, 3, 177 (1931).

(7) "Methods of the Chemists of the U. S. Steel Co. for the Sampling and Analysis of Gases," Fig. 2, p. 8.

Description of Diffusion Apparatus.—The device which was used is shown in Fig. 3. It consists of a Shaw filter flask, into which a metal orifice cup has been fitted and held in place by rubber. This is in turn closed by a rubber stopper which fits into the wide opening of the orifice cup, of which the orifice plate is the bottom. The side neck serves as the filling and flushing connection and the bottom serves for the connection to the leveling bottle containing the confining liquid. The stopcock in the bottom is very convenient in handling the device. The diameter of the orifice is 2.44 mm. in a plate 2.15 mm. thick. It is essential that there be no narrow tube leading to or from it, since this sets up extra resistance by providing a region on either side of the orifice in which an appreciable gradient is maintained so that diffusion is hindered.

Operation of Diffusion Equipment.—The diffusion apparatus was operated as follows. The confining liquid used was water. This was saturated with the gas to be used by allowing the apparatus to stand for several hours filled with a sample of the gas. Occasional shaking was employed. A fresh sample of the gas was then placed in the apparatus and the device set in a thermostat at 25° for the duration of the run. The orifice was opened, the gases allowed to diffuse for 195 minutes, the orifice closed and the sample withdrawn for combustion analysis. The volume of sample used was 250 cc. The time of 195 minutes was chosen because in that time approximately 80% of the methane will have diffused. The figure of 80% is a compromise between errors caused by general difficulties in securing complete combustion on small residues from more complete diffusion and normal experimental errors in Δn which have a greater relative value as the magnitude of Δn is decreased. As both the gas inside and the air outside were essentially saturated with water vapor, no correction for humidity was made. Barometric fluctuations were disregarded; the average barometric pressure was 620 mm.

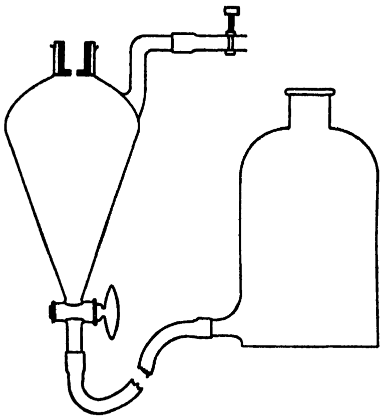

Fig. 3.—Diffusion apparatus.

Experimental Data.—Table I shows the experimental data and the data calculated from the diffusion equations for the different mixtures of gases which were employed.

The difference between the calculated and observed values are all within the probable limits of experimental error. A brief comparison of Table I

TABLE I

Composition of the gas CH_4	C_2H_6	C_3H_8	C_4H_{10}	n_0	n	Δn Obs.	Δn Calcd.
100	..	..	..	1.00	1.00	0.00	0.000
90	10	..	..	1.10	1.14	.04	.056
90	..	10	..	1.20	1.34	.14	.156
80	10	10	..	1.30	1.48	.18	.170
90	..	..	10	1.30	1.55	.25	.264
40	60	..	..	1.60	1.69	.09	.100
60	20	20	..	1.60	1.84	.24	.223
80	..	..	20	1.60	2.03	.43	.407
..	100	..	..	2.00	2.00	.00	.000

with the charts will show the degree of accuracy of the analyses based upon diffusion much better than any written explanation. Only samples were employed in which the average value of *n* is less than two for two reasons: first, most samples of natural gas fall in this region; and second, the experimental error is higher for values of *n* appreciably over two because of the form of the equations for the determination of *n*.

The equations and diagrams are based on the assumption of a pure paraffin hydrocarbon mixture. Small amounts of other gases will not have any great effect on the value of Δn. In order to minimize the effects of interference of different types of molecules, any gas which does not consist mainly of paraffin hydrocarbons should be treated to remove these other constituents before placing it in the diffusion apparatus. Impurities which consist of air or nitrogen need not be removed. Calculations show that since these gases are already considered in the diffusion equations, even large quantities of them in the original mixture will change the value of Δn by an amount considerably less than the average experimental error.

Theoretical Considerations of the Diffusion Equations and Charts

Derivation of an Equation for the Diffusion Coefficient.—For the coefficient of diffusion D_{12} for two gases diffusing into each other, Maxwell[8] modified the Meyer diffusion formula

$$D_{12} = \frac{1}{3(\nu_1 + \nu_2)} [\bar{C}_1\lambda_1\nu_2 + \bar{C}_2\lambda_2\nu_1] \qquad (1)$$

λ_1 and λ_2 are the expressions for the mean free paths of the two species of molecules from which the terms involving collisions between the same species of molecules are neglected because such collisions should not affect diffusion, as the total forward momentum is not changed. $\bar{C}_1$ and $\bar{C}_2$ are the average velocities of the molecules, and ν_1 and ν_2 their respective molecular concentrations. Substituting the values for the mean free path, Maxwell obtained

$$D_{12} = \frac{1}{3\nu_0\pi}\left[\frac{\bar{C}_1}{S_{12}^2\sqrt{1 + M_1/M_2}} + \frac{\bar{C}_2}{S_{12}^2\sqrt{1 + M_2/M_1}}\right] \qquad (2)$$

M_1 = mol. wt. of gas 1; M_2 = mol. wt. of gas 2
S_{12} = sum of radii of molecules of gas 1 and 2

We have generalized the above formula to apply to a mixture of *s* gases, $s - 1$ of which are diffusing in one direction while the other gas is diffusing in the opposite direction.

$$D_{mk} = \frac{1}{3\nu_0\pi}\left[\frac{\bar{C}_m}{\Sigma_1^{s-1}\,\alpha_s S_{ms}^2\sqrt{1 + M_m/M_s} + \alpha_k S_{mk}^2\sqrt{1 + M_m/M_k}} + \frac{\bar{C}_k}{\Sigma_1^{s-1}\,\beta_s S_{ks}^2\sqrt{1 + M_k/M_s} + \beta_m S_{km}^2\sqrt{1 + M_k/M_m}}\right] S \neq M \qquad (3)$$

The subscript *s* represents the general gas diffusing in one direction
The subscript *k* represents the gas diffusing in the opposite direction

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[8] Maxwell, "Coll. Scientific Papers," Vol. I, p. 392, and Vol. II, pp. 57 and 345; see also Jeans, "Dynamical Theory of Gases," Cambridge University Press, Cambridge, 1921, p. 315.

The subscript m represents the particu'ar one of the s gases for which the diffusion coefficient is to be calculated.

α_s = mole fraction of gas s, calculated by omitting gas m
β_s = mole fraction of gas s, calculated by omitting gas k
α_k = mole fraction of gas k, calculated by omitting gas m
β_m = mole fraction of gas m, calculated by omitting gas k

These mole fractions are the average mole fractions taken over the whole diffusion column.

This equation is obtained by integrating the simultaneous partial second order differential equations as obtained from Meyer's theory[9] of gas diffusion using assumptions similar to those Maxwell used in his equation and also with the additional assumption that there is no net motion of translation of any constituent except the two for which the diffusion constant is to be determined.[10]

M. J. Stefan[11] has developed a theory covering the diffusion of any number of constituents; but it is based on the hydrodynamical rather than the kinetic hypothesis.

Rigorous mathematical analyses for the determination of diffusion coefficients are given by Chapman[12] and by Enskog.[13] They involve the assumption of a definite molecular model (elastic spheres, point centers of force repelling according to an inverse power law, or others). Their formulas are very laborious for numerical computation.

The Diffusion Equation.—The form for the coefficient given in equation (3) is for steady flow. As the apparatus does not employ steady flow, the logarithmic mean of the initial and final concentrations of each constituent is used as the proper concentration for the calculation of the mole fraction. The ordinary diffusion equation

$$\partial A/\partial t = D\partial^2 A/\partial x^2 \tag{4}$$

upon integration gives

$$A = A_0e^{-Dt} \tag{5}$$

provided we assume that the concentration inside the apparatus remains essentially uniform and that the size of the orifice is large in comparison to the mean free path. The second of these statements tends to invalidate the first, but the actual results obtained indicate that the concentration gradient in the body of the diffusion apparatus is small enough to be neglected, since the cross sectional area is large as compared to that of the orifice.

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(9) Jeans, "Dynamical Theory of Gases," pp. 307 and 312.

(10) It is realized that this equation is complicated for calculation but such simple relations as that of Graham, that rates of diffusion are inversely proportional to the square root of the densities, do not even approximately apply to the interdiffusion of gases; for instance two gases of the same density, ethylene and nitrogen, have coefficients of diffusion into hydrogen of 0.486 and 0.674, respectively. See "Int. Crit. Tables," Vol. V, p. 62. By Graham's law of diffusion these gases would diffuse at the same rate.

(11) Stefan, *Sitsb. Akad. Wiss. Wien, Math-naturw. Klasse*, **63**, 63–124 (1871).

(12) Chapman, *Trans. Roy. Soc.* (London), **A217**, 166 (1917).

(13) Enskog, Inaug. Dissertation, Upsala, 1917, see Jeans, "Dynamical Theory of Gases," p. 319.

Derivation of an Expression for Δn.—The average number of carbon atoms per molecule is

$$n = An_a/V + Bn_b/V + Cn_c/V + \ldots \qquad (6)$$

A, B, C, etc., represent the concentrations of the various hydrocarbons, V being the sum of the concentrations of all the hydrocarbons and n_a, n_b, etc., the average number of carbon atoms per molecule of the corresponding hydrocarbons. We shall hereafter consider constituent A to be methane, B to be ethane, C propane, D n-butane, etc., for the normal paraffin hydrocarbons. We shall indicate initial concentrations and conditions by a subscript 0.

$$n_0 = A_0 + 2B_0 + 3C_0 + \ldots/V_0 \qquad (7)$$

and n at any time t

$$n = A + 2B + 3C + \ldots/V \qquad (8)$$

Then $\Delta n = n - n_0$, the increase in the average value of n during diffusion is given by the difference of equations (8) and (7). From a knowledge of the initial concentrations and the numerical values for the diffusion coefficients, the value of Δn may be calculated. The triangular diagrams are plotted from data of this type.

Numerical Illustration.—A numerical illustration of the calculation is given to make the method entirely clear. For purposes of numerical calculation equation (3) may be rewritten in the form

$$D_{mk} = \frac{\overline{C}}{\Sigma_1^{s-1}\alpha_s\varphi_{ms} + \alpha_k\varphi_{mk}} + \frac{\overline{C}_k}{\Sigma_1^{s-1}\beta_s\varphi_{ks} + \beta_m\varphi_{km}} \qquad (9)$$

The numerical values of the terms together with their equivalents in eqn. (3) are given in Table II. The numerical values for $\overline{C}_m$ and $\overline{C}_k$ include the constant factors, those from the equation, those depending on the size of the apparatus, and those depending on the units used. The time of the runs (195) minutes is considered as the unit of time, $t = 1$.

A pure hydrocarbon gas composed of 60% methane, 20% ethane and 20% propane will be considered.

To calculate D_{ak} the appropriate values are substituted in equation (9). All the quantities are given in Table II except the values of the coefficients representing mole fractions. From similar runs we know that only approximately 0.25 of the methane, 0.36 of the ethane and 0.45 of the propane are left at the end of the run. Initial and final concentrations together with the log mean of the concentrations of the gases are as follows.

	Methane	Ethane	Propane
Initial	60.0	20.0	20.0
Final	15.0	7.2	9.0
Log mean	32.3	12.5	13.8

For the calculation of the diffusion coefficient D_{ak} eqn. (9) is used replacing m by a (a represents methane).

$\alpha_b = 12.5/126.3$ $\alpha_c = 13.8/126.3$ $\alpha_k = 100.0/126.3$
$\beta_a = 32.3/58.6$ $\beta_b = 12.5/58.6$ $\beta_c = 13.8/58.6$

The quantities $e^{-D_{ak}t}$, $e^{-D_{bk}t}$, and $e^{-D_{ck}t}$ are found to be 0.252, 0.396 and 0.467, respectively. This means that 25.2% of the methane, 39.6% of the ethane and 46.7% of the propane remain. Now in order to obtain greater accuracy we recalculate the values for the diffusion coefficient using the 25.2, 39.6 and 46.7% instead of the 25, 36 and 45% figures previously used. This gives $D_{ak} = 1.374$. Similarly D_{bk} and D_{ck} are found to be 0.924 and 0.753, respectively. Substitution in equation (7) gives

TABLE II

$\varphi_{AK} = 18.6 = S_{ak}^2 \sqrt{1 + M_a/M_k}$

$\varphi_{AB} = 25.7 = S_{ab}^2 \sqrt{1 + M_a/M_b}$

$\varphi_{AC} = 29.5 = S_{ac}^2 \sqrt{1 + M_a/M_c}$

$\varphi_{AD} = 33.1 = S_{ad}^2 \sqrt{1 + M_a/M_d}$

$\varphi_{BK} = 28.0 = S_{bk}^2 \sqrt{1 + M_b/M_k}$

$\varphi_{BA} = 35.2 = S_{ba}^2 \sqrt{1 + M_b/M_a}$

$\varphi_{BC} = 40.5 = S_{bc}^2 \sqrt{1 + M_b/M_c}$

$\varphi_{BD} = 44.0 = S_{bd}^2 \sqrt{1 + M_b/M_d}$

$\varphi_{CK} = 37.9 = S_{ck}^2 \sqrt{1 + M_c/M_k}$

$\varphi_{CA} = 48.9 = S_{ca}^2 \sqrt{1 + M_c/M_a}$

$\varphi_{CB} = 48.8 = S_{cb}^2 \sqrt{1 + M_c/M_b}$

$\varphi_{CD} = 55.2 = S_{cd}^2 \sqrt{1 + M_c/M_d}$

$\varphi_{DK} = 48.3 = S_{dk}^2 \sqrt{1 + M_d/M_k}$

$\varphi_{DA} = 63.0 = S_{da}^2 \sqrt{1 + M_d/M_a}$

$\varphi_{DB} = 61.3 = S_{db}^2 \sqrt{1 + M_d/M_b}$

$\varphi_{DC} = 63.2 = S_{dc}^2 \sqrt{1 + M_d/M_c}$

$\varphi_{KA} = 25.2 = S_{ka}^2 \sqrt{1 + M_k/M_a}$

$\varphi_{KB} = 27.5 = S_{kb}^2 \sqrt{1 + M_k/M_b}$

$\varphi_{KC} = 30.7 = S_{kc}^2 \sqrt{1 + M_k/M_c}$

$\varphi_{KD} = 34.3 = S_{kd}^2 \sqrt{1 + M_k/M_d}$

$\bar{C}_a = 18.0$

$\bar{C}_b = 13.2$

$\bar{C}_c = 10.9$

$\bar{C}_d = 9.5$

$\bar{C}_k = 13.4$

The molecular radii used in the above calculations are: air, 1.87×10^{-8}, CH_4, 2.00×10^{-8}; C_2H_6, 2.56×10^{-8}; C_3H_8, 3.02×10^{-8}; and C_4H_{10}, 3.42×10^{-8} cm. The value for air was taken from Jeans, "Dynamical Theory of Gases," p. 327. We calculated the others from Trautz's viscosity data [Max Trautz, *Ann. Physik*, [5] **10**, 81–96 (1931)]. Those for methane and ethane agree very closely with diameters calculated from diffusion coefficients for different pairs of gases taken from "Int. Critical Tables," and calculated by means of the Stefan–Maxwell equation (equation (2)).

$$n_0 = (60 \times 1 + 20 \times 2 + 20 \times 3)/100 = 1.6 \qquad (10)$$

and in equation (8)

$$n = \frac{A + 2B + 3C}{V} = \frac{A_0e^{-D_{ak}t} + 2B_0e^{-D_{bk}t} + 3C_0e^{D_{ck}t}}{A_0e^{-D_{ak}t} + B_0e^{-D_{bk}t} + C_0e^{-D_{ck}t}} = 1.823 \qquad (11)$$

$$\text{Therefore: } An = n - n_0 = 0.223 \qquad (12)$$

Summary

1. An extension of the Maxwell diffusion equation has been made to apply to a mixture of gases diffusing out through an orifice, which is large in comparison to the mean free path, against air diffusing in at barometric pressure and constant temperature.

2. An inexpensive device which is simple to operate has been developed.

3. The apparatus and equations have been checked by application to known mixtures of paraffin hydrocarbons.

4. Charts have been developed for the use of this information in gas analysis, whereby a much closer approximation to the actual paraffin hydrocarbons can be obtained by a combination of the diffusion apparatus

with the absorption and slow combustion equipment than can be obtained without the diffusion apparatus.

Golden, Colorado

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[Contribution from the Chemical Laboratories of Duke University and Randolph Macon Woman's College]

Dipole Moment and Group Rotation. I. The Moments of the Chloro- and Nitrobenzyl Chlorides and the Effect of Group Separation[1]

By J. M. A. de Bruyne, Rose M. Davis and Paul M. Gross

Discussion of the effect of rotation of component dipoles within molecules on their dipole moments has been confined largely to substituted straight chain hydrocarbons with two identical polar groups at each end. Ethylene chloride is the simplest case. By increasing the length of the hydrocarbon chain, it has been sought to separate the like polar groups at its ends and so study their interactions as a function of the distance separating them.[2]

Unless an extended zigzag chain is assumed with the polar groups rotating about its ends, the number of possible configurations such a molecule can assume by rotation about the various bonds is very great, so that conclusions concerning the interaction of the polar groups as affected by their separation must be drawn with considerable reservation.

The substituted benzyl halides are compounds in which this uncertainty is eliminated, since the benzene ring fixes the position of the second polar group and defines its separation from the rotating halide group in the side chain. This paper gives the results of the determination of the dipole moments of the ortho, meta, and para chlorobenzyl chlorides and the ortho and meta nitrobenzyl chlorides in different solvents. These are the first of a series of measurements designed to extend broadly the experimental background of this field by measuring the dipole moments of molecules containing varying types of rotating groups located at different distances apart in the molecule.

Method.—The dielectric constant ϵ, density d, and refractive index for the sodium D line n_D were determined for dilute solutions of these compounds at 30 ± 0.01°. The molar polarization P_2 of the solute at each concentration was calculated from the equation of Debye[3] in the form

$$P_2 = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{M_2}{d}\,\frac{w_1 + w_2}{w_2} - \frac{w_1}{w_2}\,\frac{M_2}{M_1}\,P_1 \qquad (1)$$

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[1] Part of a thesis submitted by J. M. A. de Bruyne in partial fulfilment of the requirements for the Ph.D. degree in Chemistry at Duke University, in June, 1932.

[2] Compare Smyth and Walls, This Journal, 54, 2261 (1932).

[3] Debye, "Polar Molecules," Chemical Catalog Co., New York, 1929, p. 45.

in which w_1 and w_2 are the weights, and M_1 and M_2 the molecular weights of the solvent and solute, respectively, and P_1 is the molar polarization of the solvent. The molar refraction R_2 of the solute was calculated by substituting for ϵ the square of the refractive index for the sodium D line in equation (1), and for P_1, the molar refraction of the solvent R_1 for the sodium D line. By plotting the values of P_2 against the mole fraction c_2 of the solute and extrapolating to $c_2 = 0$, the molar polarization of the solute P_∞ at infinite dilution was found. The dipole moment μ was then calculated from the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - R_2)T} \text{ e. s. u.} \qquad (2)$$

Apparatus.—The dielectric constants were determined by the heterodyne beat method employing an arrangement of apparatus similar to that of Williams and Weissberger[4] and others.[5]

A plate-tuned circuit was used in each oscillator so that the various condensers could be grounded, and the entire electrical system was carefully shielded. The beat note was matched with the 1000-cycle note of an electrically excited fork.

The standard condenser was a General Radio Company Precision Condenser, of 500 mmf. capacitance, with a scale of 2500 divisions, and was calibrated by a step method.[6]

Capacitance measurements were made at a frequency of 10^6 cycles/sec.

The measuring condenser was of brass, gold plated, and consisted of three concentric cylinders in an outer brass container. These were mounted by rods on a bakelite lid machined to fit the brass container which was at ground potential. The inner and outer cylinders were connected together. A switch was so arranged that it could connect the middle cylinder either to this pair or to the container, thus providing a minimum or maximum capacitance. The difference between the two values (approximately 100 mmf. air capacitance) measured in corrected scale readings of the standard condenser was used in calculating the dielectric constant. This type of measurement eliminated any uncertainty from lead corrections and also the errors due to changes in the frequency of the oscillators with time.

A correction was necessary for the capacitance of that part of the condenser above the liquid level and due mainly to the rods with the bakelite of the lid as dielectric between them. As this was constant, it was evaluated by obtaining the difference values of the condenser for the standards dry air and benzene. The correction k so found was approximately 6% of the difference value for air. The dielectric constant ϵ of a liquid was then calculated from the equation

$$\epsilon = (\Delta S + k\epsilon')/(\Delta S' + k) \qquad (3)$$

in which ΔS and $\Delta S'$ represent the difference values in corrected scale readings for the liquid and for the standard, respectively, and ϵ' the dielectric constant of the standard.

Such difference measurements made on two portions of the standard condenser scale agreed within 1 part in 3000 in every case, and in most instances were within one part in 5000.

Materials

Benzene.—Kahlbaum best grade of benzene was dried over phosphorus pentoxide and fractionated in a Dufton still with a 1.8-m. column. The main fraction distilling within 0.01° range was fractionally crystallized until a fraction of maximum freezing temperature was obtained. Benzene freezing within 0.02° of this temperature was used as the solvent. It was distilled from freshly cut sodium when needed: b. p. 80.05°; $n^{30°}_D$ 1.49486; d^{30}_4 0.86840 (average).

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[4] Williams and Weissberger, THIS JOURNAL, 50, 2332 (1928).

[5] Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, New York, 1931, p. 54.

[6] Compare Linton and Maass, THIS JOURNAL, 53, 957 (1931).

Heptane.—Heptane from the Ethyl Gasoline Corporation was shaken with concentrated sulfuric acid, sodium hydroxide, mercury and distilled water, then dried over calcium chloride, over phosphorus pentoxide, and then fractionated. The fraction used had the constants: b. p. 98.47–98.52°; n^{30}_D 1.38292; d^{30}_4 0.67520.

Carbon Tetrachloride.—Eastman best grade was fractionated twice, giving material with the constants: b. p. 76.74°; n^{30}_D 1.45454; d^{30}_4 1.5747.

o-Chlorobenzyl Chloride.—Four hundred and fifty grams from Eastman Kodak Company was repeatedly fractionated at reduced pressure in a Hickman still. Forty-five grams of liquid boiling between 109.0 and 109.2° at 25.6 mm. was obtained. A chlorine analysis of the compound was made by the method described by Vaughn and Nieuwland:[7] chlorine found, 44.02; calcd., 44.05.

m-Chlorobenzyl Chloride.—This was prepared by chlorinating *m*-chlorotoluene. The liquid after shaking with potassium carbonate solution and drying over potassium carbonate and calcium chloride, was fractionated at reduced pressure. The sample used boiled at 111.0–111.2° at 25.4 mm.

p-Chlorobenzyl Chloride.—A sample from Eastman Kodak Company was fractionally crystallized and distilled at reduced pressure. The best fraction obtained after repeated fractionation froze between 28.2–28.4°; b. p. 114.0° at 25 mm.

The total chlorine content was determined by Vaughn and Nieuwland's method: chlorine found, 43.82, 43.91; calcd., 44.05. Side chain chlorine was determined by hydrolysis with alcoholic potassium hydroxide and subsequent analysis of the aqueous solution for chlorine: chlorine found, 22.4; calcd., 22.0. Oxidation of a sample of the compound by refluxing with alkaline permanganate solution gave the anticipated *p*-chlorobenzoic acid. These tests, which seemed desirable because of the results reported by Bergmann and Engel[8] for this substance, conclusively established the identity and purity of our sample of *p*-chlorobenzyl chloride.

o-Nitrobenzyl Chloride.—A sample from the British Drug Houses, Ltd., was recrystallized first from ligroin and then fractionally crystallized. A sample with f. p. 48.0–48.25° was used.

m-Nitrobenzyl Chloride.—A sample similar to the ortho compound was obtained by the same method and had f. p. 45.15–45.35°.

Results

As a check on the apparatus and method the dipole moment of chlorobenzene was determined in benzene as solvent and was found to be $\mu = 1.56D$,[9] a value identical with that found by other recent workers.

The data for the concentrations, dielectric constants and refractive indices of the solutions of the compounds are given in Table I and the polarizations and dipole moments are summarized in Table II. Bergmann and Engel[8] have determined the moment of *p*-chlorobenzyl chloride and find $\mu = 2.11D$. This value is so different from that found here ($\mu = 1.71D$ in benzene) that we are led to conclude that Bergmann and Engel were either dealing with some other substance or that there was some un-

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(7) Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

(8) Bergmann and Engel, *Z. physik. Chem.*, [B] **15**, 85 (1931).

(9) We will designate the values of the moments in terms of the Debye (*D*) as suggested in the "Physikalisch-chemisches Taschenbuch," S. Hirzel, Leipzig, 1932, Vol. I, p. 123, and accepted by others. (Compare Weissberger and Sängewald, *Z. physik. Chem.*, [B] **20**, 145 (1933).) $1D = 1 \times 10^{-18}$ e. s. u.

explained source of error in their measurements on this compound. Our values in the three different solvents agree well and are also practically the same as those for the similar compounds *p*-bromobenzyl chloride (μ = 1.71*D*) and *p*-chlorobenzyl bromide (μ = 1.72*D*) measured by Smyth and Walls,[10] as would be expected from the closeness of the values of the C–Cl and C–Br vector moments. The identity and purity of our sample seems well established as previously noted (see. p. 3938).[11] Moreover, a molecular weight determination in benzene solution by the freezing point method gave a value 158.8 as compared to the theoretical value 161.0.

Values for the dipole moments of the other substances have not been reported previously.

Discussion

An exact treatment of the observed moments of the compounds measured here by the method of group moments of Eucken and Meyer[12] should also take into account the moments induced in any one bond by all others following the procedure of Smallwood and Herzfeld.[13] Such an exact treatment has been applied to these compounds but to avoid duplication it will be reserved for presentation in a later paper along with the results of measurements of the moments of bromo and iodo substituted compounds of the benzyl halide type. The induction effects are more important in these cases because of the larger polarizabilities of the C–Br and C–I group moments.

In the present paper we will follow a procedure which gives a good approximation to this more rigorous treatment in the cases of the para and meta substituted benzyl chlorides. Its use is possible because calculation shows that as the —CH_2Cl group assumes various rotational positions, the moment induced in it and the moments induced by it are practically constant in value when the ring substituent is in either para or meta position.

The observed moment of benzyl chloride,[14] μ = 1.85*D*, which is well established experimentally, may be regarded as representing the resultant of all the inherent bond moments and all the induced moments in the ring and side chain. Similarly the observed moment (μ = 1.56*D*) of chlorobenzene is the resultant of all the inherent bond moments and the induced moments in the molecule. If the direction of the vector representing the benzyl chloride molecule were known, it would be possible to combine it vectorially with the observed vector for chlorobenzene and obtain the moment of *p*-chlorobenzyl chloride, because the slight difference in induction effects of the chlorine and —CH_2Cl groups, respectively, on the groups para to them are negligible. By using the observed value μ = 1.70*D* for *p*-chlorobenzyl chloride together with those of chlorobenzene and benzyl chloride it is possible to calculate the direction of the benzyl chloride vector

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[10] Smyth and Walls, THIS JOURNAL, **54**, 1860 (1932).

[11] As this manuscript was being submitted for publication a determination of this moment in benzene appeared by Weissberger and Sängewald [*Z. physik. Chem.*, **B20**, 148 (1933)]. They find μ = 1.74*D*, in excellent agreement with our value of μ = 1.71*D*.

[12] Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

[13] Smallwood and Herzfeld, THIS JOURNAL, **52**, 1919 (1930).

[14] Smyth, Ref. 5, p. 203.

Table I

c_2	d	ϵ	P_2	n_D	R_2
o-Chlorobenzyl chloride–benzene					
0.0000	0.86836	2.2626		1.49486	
.0048221	.87108	2.3018	157.0	1.49543	42.3
.009941	.87398	2.3441	157.2	1.49587	41.5
.014905	.87670	2.3842	156.3	1.49628	41.4
.020187	.87960	2.4274	155.3	1.49670	41.3
.025262	.88240	2.4694	154.7	1.49739	41.7
o-Chlorobenzyl chloride–carbon tetrachloride					
0.00000	1.57471	2.2149		1.45454	
.0029367	1.57361	2.2351	149.1	1.45494	41.0
.005783	1.57255	2.2550	149.6	1.45536	41.1
.0088668	1.57133	2.2764	149.4	1.45568	40.6
.011665	1.57020	2.2960	149.3	1.45604	40.8
*.015042	1.56888	2.3195	148.9	1.45676	41.7
o-Chlorobenzyl chloride–heptane					
0.0000	0.67519	1.9030		1.38292	
.002926	.67675	1.9147	144.5		
.006035	.67834	1.9273	145.2	1.38374	39.5
.009375	.68002	1.9415	147.7	1.38422	40.1
.012244	.68152	1.9528	146.1	1.38470	40.8
.018312	.68467	1.9786	146.8	1.38565	41.0
m-Chlorobenzyl chloride–benzene					
0.0000	0.86843	2.2627		1.49490	
.004397	.87085	2.2890	126.3		
.008926	.87339	2.3165	126.4	1.49547	40.1
.01489	.87664	2.3511	124.7	1.49613	41.1
.02402	.88151	2.4045	123.7	1.49686	41.2
.03992	.89006	2.5004	123.1	1.49816	41.1
m-Chlorobenzyl chloride–carbon tetrachloride					
0.0000	1.5747	2.2157		1.45454	
.004009	1.5731	2.2381	127.2	1.45501	39.3
.008102	1.5714	2.2601	126.4	1.45558	41.0
.01212	1.5698	2.2817	125.5	1.45616	41.2
.02011	1.5666	2.3253	124.9	1.45738	41.7
.03534	1.5607	2.4083	123.5	1.45959	41.5
m-Chlorobenzyl chloride–heptane					
0.0000	0.67523	1.9025		1.38292	
.004147	.67729	1.9168	130.3	1.38332	37.9
.007952	.67936	1.9299	128.9	1.38398	39.6
.01200	.68141	1.9435	127.6	1.38453	40.0
.01977	.68533	1.9702	127.3	1.38574	40.9
.034619	.69298	2.0217	126.3	1.38836	42.0

TABLE I (*Concluded*)

c_2	d	ϵ	P_2	n_D	R_2
p-Chlorobenzyl chloride–benzene					
0.0000	0.86836	2.2627		1.49491	
.005037	.87115	2.2840	100.5	1.49536	40.8
.010272	.87399	2.3067	101.2	1.49577	41.3
.015503	.87683	2.3287	100.6	1.49603	40.7
.02064	.87956	2.3509	100.8	1.49647	40.8
.02586	.88238	2.3727	100.4	1.49695	41.1
p-Chlorobenzyl chloride–carbon tetrachloride					
0.0000	1.5746	2.2157		1.45454	
.003062	1.57345	2.2277	101.0	1.45483	38.8
.006025	1.57223	2.2394	101.8	1.45529	40.9
.008808	1.57115	2.2501	101.4	1.45564	40.7
.01246	1.56962	2.2653	101.6	1.45624	41.3
.01511	1.56858	2.2749	100.7	1.45663	41.5
p-Chlorobenzyl chloride–heptane					
0.0000	0.67522	1.9032		1.38292	
.005002	.67778	1.9154	99.2	1.38358	39.7
.009921	.68030	1.9275	100.0	1.38431	40.6
.01481	68276	1.9393	99.7	1.38512	41.4
.01988	.68536	1.9521	100.0	1.38588	41.5
o-Nitrobenzyl chloride–benzene					
0.0000	0.86841	2.2627		1.49486	
.0009047	.86902	2.2840	385.4		
.002973	.87042	2.3323	379.9	1.49515	41.6
.004429	.87138	2.3665	378.0	1.49536	42.7
.006026	.87247	2.4037	374.7	1.49554	42.4
.007489	.87349	2.4383	372.8	1.49573	42.2
o-Nitrobenzyl chloride–carbon tetrachloride					
0.0000	1.57469	2.2157		1.45430	
.002474	1.57394	2.2638	354.1	1.45470	42.3
.003950	1.57349	2.2926	352.5	1.45503	43.9
.005491	1.57311	2.3234	352.5	1.45526	43.2
.006936	1.57270	2.3514	349.7	1.45560	43.9
m-Nitrobenzyl chloride–benzene					
0.0000	0.86842	2.2627		1.49491	
.001934	.86973	2.3024	339.6	1.49517	42.4
.002794	.87029	2.3197	337.0	1.49523	42.4
.005889	.87238	2.3829	333.1	1.49562	42.5
.008984	.87445	2.4459	329.0	1.49598	42.5
.01183	.87641	2.5055	327.3	1.49627	42.2
m-Nitrobenzyl chloride–carbon tetrachloride					
0.0000	1.57475	2.2157		1.45436	
.001515	1.57425	2.2445	348.7	1.45466	44.2
.003010	1.57378	2.2729	346.7	1.45486	43.0
.004437	1.57335	2.2992	341.8	1.45509	43.1
.005988	1.57298	2.3283	339.3	1.45539	42.9
.007438	1.57259	2.3558	337.2	1.45577	43.9

Table II

	Solvent	P_2^∞	$P_2^\infty - R_2$	$\mu \times 10^{18}$
o-Chlorobenzyl chloride	Benzene	158.0	116.5	2.39
	CCl_4	149.5	108.5	2.30
	Heptane	144.2	103.5	2.25
m-Chlorobenzyl chloride	Benzene	126.8	85.9	2.05
	CCl_4	127.1	85.8	2.05
	Heptane	129.8	89.1	2.09
p-Chlorobenzyl chloride	Benzene	100.9	60.0	1.71
	CCl_4	101.6	60.5	1.72
	Heptane	99.4	58.6	1.69
o-Nitrobenzyl chloride	Benzene	385.6	343.4	4.10
	CCl_4	355.6	312.4	3.91
m-Nitrobenzyl chloride	Benzene	341.4	299.0	3.82
	CCl_4	352.4	309.0	3.89

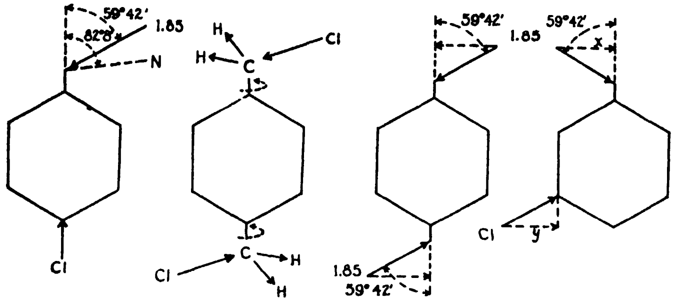
Table III

Compound	Av. obs. moment	Calcd. moment	Angle	Distances, Å.	
				Min.	Max.
p-Xylylene dichloride	2.23	2.26	59°42′	6.34	6.50
m-Chlorobenzyl chloride	2.06	2.10	59°42′	4.36	4.95
m-Nitrobenzyl chloride	3.86	4.01	63°46′	4.36	4.95
o-Chlorobenzyl chloride	2.31	2.70	59°42′	2.38	3.33
o-Nitrobenzyl chloride	4.00	4.75	63°46′	2.38	3.33

whose magnitude is 1.85*D*. This is in effect an evaluation of the constant contribution that a —CH_2Cl group attached to a phenyl group will make to the observed moment of a compound of which it is a part. This contribution will be constant in compounds with ring substituents para or meta to the —CH_2Cl group provided the moments of such substituent groups are not so large as to induce moments of appreciable magnitude in the —CH_2Cl group. These induced moments will be proportional to the inverse cube of the distance and for the separations involved in the meta and para cases will be small and will not vary greatly with rotation.

Under these assumptions we have calculated the angle as 59°5′ that the vector 1.85 makes with the vertical axis of the ring as shown in Fig. 1(a). The moment of benzyl chloride as calculated from the group moments of Eucken and Meyer is 1.86*D*, disregarding induced effects, and makes an angle of 82°8′ as shown by the dotted line N of Fig. 1(a). The tilt upward by 22° to the angle 59°5′ is a measure of the induced moments in the molecule. It is to be emphasized that this tilting does not necessarily imply any distortion of the normal carbon valence angles but simply determines the direction of the resultant vector of the benzyl chloride molecule relative to the axis of the ring passing through the carbon linked to the —CH_2Cl group.

Since in the para compounds the separation between the dipole of the para group and that of the C–Cl bond of the —CH_2Cl group is constant and independent of rotation, then the angle for this vector calculated for different para substituted benzyl chlorides should remain substantially unchanged. Such is the case. Using the moments of *p*-bromobenzyl chloride ($\mu = 1.70D$) and *p*-nitrobenzyl chloride ($\mu = 3.58D$) and the group moments C–Br = $1.50D$ and C–NO_2 = $3.99D$,[15] values for this angle of 60°19′ and 63°46′, respectively, are found showing that the angle is altered but little by the nature and degree of polarity of the para substituent.



(a) (b) (c) (d)

Fig. 1.

This angle, having been shown to be constant, may be used to calculate the moments of compounds containing the rotating —CH_2Cl group of the type shown in Fig. 1(b and d) where the effective component group moments are resolved into their respective vertical vectors and the horizontal rotating vectors x and y. If the effective mean of the latter for all rotational positions can be evaluated, it can be combined with the net vertical component to give the resultant moment of the molecule. For the assumption that all rotational positions are equally probable the effective mean of the two horizontal components is found from

$$\mu_H = \sqrt{\frac{1}{\pi}\int_0^\pi (x^2 + y^2 + 2xy\cos\Theta)d\Theta} = \sqrt{x^2 + y^2} \qquad (4)$$

where Θ is the angle between the two considered as rotating independently in the same plane.

In the case of the compound *p*-xylylene dichloride (Fig. 1b and c), the vertical components cancel and the moment can be found directly from equation (4), each horizontal component being equal to 1.85 sin 59°42′. This is the average angle found from the observed moments of *p*-chloro- and *p*-bromobenzyl chloride. The value so calculated is $\mu = 2.26D$, in excellent agreement with the observed value $\mu = 2.23D$.[16]

Calculations similar to these have been applied to those molecules measured here whose moments depend on rotation, the results of which are

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(15) The average of recent values. See Smyth, Ref. 5, pp. 195 and 203. For the moments of the para compounds see Ref. 10.

(16) Weissberger and Sängewald, *Physik. Z.*, **30**, 792 (1929). A result similar to ours for the calculated moment is given by these authors (see Ref. 11).

given in Table III together with the angles employed. The agreement in the case of the meta chloro- and nitrobenzyl chlorides is good and may, if the validity of the approximate treatment used is granted, be taken as evidence that rotation in these compounds is practically free and unhindered. The large divergence in the case of the ortho compounds between calculated and observed values would on the same basis be attributed to hindrance of free rotation but is probably also due to the failure of the present treatment to weight correctly the induced effects in the ortho cases.

The relation of the separation of the principal dipoles to these results is seen from the last two columns of Table III. These give the maximum and minimum distances in Å. between these dipoles which are assumed to be located at the periphery of the carbon atoms concerned.[17] The table shows that there is practically free rotation when the principal dipoles do not approach each other closer than 4.4 Å. Even with approach of the dipoles to within about 3 Å. of each other in the ortho compounds there is a reduction of moment of only about 15% of that calculated for free rotation with the treatment used here. This small difference is of doubtful significance, however, since this approximate treatment would scarcely be valid for the ortho compounds as previously indicated.

The effect of the solvent on the observed moment and its relation to the freedom of rotation is seen from Table III. In *p*-chlorobenzyl chloride where every rotational position is equally probable, practically identical moments are found in the three solvents. The moments of the meta compounds which are close to those calculated here for free rotation differ but little in the different solvents, whereas fairly large differences are found for both ortho compounds, indicating that freedom of rotation in the case of small dipole separations is significantly affected by the solvent. No systematic regularity of effect of solvent is however apparent, indicating that other factors such as slight deviations from ideality may also cause part of the observed divergences. The indications are that the absence of divergences between values obtained in different solvents may be a valuable criterion for the existence of freedom of rotation.

Summary

The dielectric constants, densities and refractive indices of dilute benzene, carbon tetrachloride and heptane solutions of ortho, meta and para substituted benzyl chlorides have been determined at 30° and also those of dilute benzene and carbon tetrachloride solutions of ortho and meta nitrobenzyl chlorides. The dipole moments of these compounds have been discussed in relation to freedom of rotation as affected by the extent of separation of the groups concerned.

DURHAM, NORTH CAROLINA

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[17] Based on the values of Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE

Phenylarsonic Acid as a Reagent for the Determination of Tin

BY J. S. KNAPPER, K. A. CRAIG AND G. C. CHANDLEE

Attention has been called to the possibilities of phenylarsonic acid as an analytical reagent in methods described by Rice, Fogg and James[1] for the determination of zirconium and thorium. The present investigation extends this study to include conditions for the separation and determination of tin.

Phenylarsonic Acid.—Eastman phenylarsonic acid was used without purification. Some samples left no non-volatile residue on ignition; others contained a small amount of sodium salts which did not interfere. A saturated aqueous solution was used as the reagent.

Tin Standards.—For the determination of tin in the absence of other metals Bureau of Standards Sample No. 42B, 99.99% tin, was used. For the determination of tin in the presence of other metallic ions Bureau of Standards Samples No. 37B, sheet brass and No. 52, cast bronze, were used. Other samples were prepared from the pure tin and purified salts of the metals.

Determination of Tin.—Samples of approximately one-tenth of a gram of the pure tin were treated with 10 cc. of 1:1 nitric acid and the mixture heated gently until the metal was completely oxidized. The heating was continued until any excess nitric acid was driven off, care being taken not to dehydrate the metastannic acid. Concentrated hydrochloric acid was then added, dropwise, until the tin was in solution. It was found that phenylarsonic acid would form a precipitate with tin in solutions which contained as much as 50% by volume of hydrochloric or sulfuric acid. However, precipitation was not quantitative when the acid concentration was greater than 5% by volume of hydrochloric acid or 7.5% by volume of sulfuric acid and reasonable amounts of reagent were used. Sufficient acid was added so that the final concentration was within these values upon dilution with water to a volume of 150–200 cc.

The tin was precipitated in hot solution by the addition of 35 cc. of the saturated aqueous solution of phenylarsonic acid. When only enough hydrochloric acid to dissolve the metastannic acid was added, about 1 cc. for this weight of tin, the solution could be filtered immediately. When acid in amounts approaching the limits indicated was added, it was necessary to allow the solution to stand for several hours before filtering. A small amount of paper pulp aided in the filtration. The precipitate was washed with a 4% solution of ammonium nitrate until free of chlorides or sulfates.

All precipitates were ignited to the oxide, no attempt being made to determine composition. The precipitate was ignited gently over a flame until all of the carbon was burned off. It was then heated in an electric furnace at a temperature of 1075–1100° to constant weight. Samples of pure stannic oxide heated under the same conditions showed no loss in weight.

Taking amounts of stannic oxide between one and three tenths of a gram and concentrations of hydrochloric acid or sulfuric acid of 2.5–5.0 and 7.5%, respectively, twelve determinations gave results with an average deviation of 1.1 parts per thousand. The somewhat higher acid concentration permissible in solutions acid with sulfuric acid may possibly be explained on the basis of a complex formed by stannic chloride with hydrochloric acid.[2]

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(1) Rice, Fogg and James, THIS JOURNAL, 48, 895 (1926).

(2) Dickinson, *ibid.*, 44, 276 (1922).

In general, completeness of precipitation depended upon the relative amounts of acid and reagent present. With acid concentrations above those given, impractical quantities of reagent were required.

Separation from Other Elements.—In aqueous solutions of the chlorides or sulfates most of the elements commonly found in alloys of tin formed precipitates with phenylarsonic acid. With aluminum salts, hydrolysis made the solution sufficiently acid to prevent precipitation. These precipitates were readily soluble in acid and quantitative separations of tin were made in solutions of brass and bronze samples in which as small an amount as one cc. of concentrated hydrochloric acid was added to the 200 cc. volume. None of the elements showed any tendency to be carried down with the tin salt except iron. The difficulty was overcome by one reprecipitation. The precipitate, after washing, was returned to the original beaker, 5 cc. of concentrated hydrochloric acid added and the mixture heated until the precipitate was disintegrated. Water was added to bring the volume to 150–200 cc. and the tin was reprecipitated with 15 cc. of the phenylarsonic acid solution. The determination was then completed in the manner described.

The results obtained for the separation of tin from varying amounts of other elements are given in Table I.

Table I

Determination of Tin in Presence of Other Elements

(a) B. of S. Sample No. 52. Cast Bronze

Sample, g.	Tin, g. (calcd.)	Tin, in sample, %	Other elements present, %		Tin found, g.	% of tin found	Diff., g.
0.5018	0.0396	7.90	Cu	88.33	0.0399	7.95	+0.0003
.5044	.0398		Zn	1.89	.0397	7.87	− .0001
.5011	.0396		Pb	1.52	.0399	7.96	+ .0003
.5081	.0401		Sb	0.16	.0404	7.95	+ .0003
.5001	.0395		Ni	0.13	.0398	7.96	+ .0003
.5073	.0401		Fe	0.12	.0400	7.89	− .0001
					Av.	7.93	

(b) B. of S. Sample No. 37b. Sheet Brass

Sample, g.	Tin, g. (calcd.)	Tin, in sample, %	Other elements present, %		Tin found, g.	% of tin found	Diff., g.
1.0066	0.0099	0.99	Cu	70.36	0.0096	0.95	−0.0003
1.0029	.0099		Zn	27.09	.0099	0.99	.0000
1.0010	.0099		Pb	0.90	.0101	1.01	+ .0002
1.0008	.0099		Ni	0.45	.0099	0.99	.0000
1.0024	.0099		Fe	0 21	.0097	0.97	− .0002
					Av.	0.98	

(c) Sample Prepared from Pure Salts

Sample, g.	Tin, g. (calcd.)	Tin, in sample, %	Other elements present, %		Tin found, g.	% of tin found	Diff., g.
0.8350	0.1002	12.00	Cu	40.00	0.0998	11.95	−0.0004
.8733	.1048		Zn	20.00	.1047	11.99	− .0001
.8733	.1048		Pb	10.00	.1045	11.97	− .0003
			Ni	4.00			
			Fe	5.00	Av.	11.97	
			Sb	5.00			
			Cd	2.00			
			Al	2.00			

Zirconium.—Conditions satisfactory for a quantitative separation of zirconium and tin by means of phenylarsonic acid could not be obtained. While the acid concentration permissible for complete precipitation of tin is fixed at 5% hydrochloric acid or

7.5% sulfuric acid, the element will precipitate to some extent when as much as 0.2 g. is present, even in solutions containing 50% by volume of either acid.

Thorium.—The determination of thorium with phenylarsonic acid was accomplished by Rice, Fogg and James[1] only in solutions containing acetic acid and ammonium acetate. However, in the present work it was found that part of the thorium was precipitated, when 35 cc. of reagent was used, in a 5% solution of hydrochloric acid. This is the upper limit of acidity permissible for the determination of tin. A satisfactory separation of tin and thorium with this reagent does not seem possible.

Bismuth.—Due to the tendency of bismuth salts to hydrolyze it was necessary to precipitate in solution containing 5% by volume of hydrochloric acid. Results were not satisfactory in sulfuric acid solution. The volume of the solution was kept at approximately 200 cc. Precipitation was done in hot solution by the addition of 40–50 cc. of the reagent and the mixture was allowed to stand several hours before filtering. Reprecipitation was not necessary. The determination was completed in the manner already described. Taking amounts of stannic oxide between one and two tenths of a gram, in the presence of approximately equal amounts of Bi_2O_3, four determinations gave results with an average deviation of two parts per thousand.

Summary

A new gravimetric method for the determination of tin has been described, in which the tin is precipitated with phenylarsonic acid. This method separates tin quantitatively from a number of elements commonly occurring with it in alloys, but not from zirconium or thorium.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Action of Hydriodic Acid on the Difficultly Soluble Sulfates[1]

BY EARLE R. CALEY

While a number of facts indicate that hydriodic acid is generally more reactive chemically than either hydrochloric acid or hydrobromic acid under like conditions, it has not been recognized that this difference is so great that a number of slightly soluble compounds, quite inert toward the latter acids, react easily with hydriodic acid, a striking example being stannic oxide.[2] In a preliminary note[3] it was stated that a number of other compounds highly resistant to hydrochloric acid, and even such active solvents as nitric acid and aqua regia, are more or less readily decomposed by hydriodic acid. This present paper contains a more detailed account of the action of the latter acid on certain of these compounds.

Materials and General Procedure.—The hydriodic acid used in the experiments was principally the constant boiling acid of specific gravity

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(1) Abstracted from a paper presented at the 85th meeting of the American Chemical Society, Washington, D. C., March, 1933.

(2) Caley, THIS JOURNAL, 54, 3240 (1932).

(3) Caley, *ibid.*, 54, 4112 (1932).

1.70, although for certain experiments acids of lower concentration were prepared from this by dilution. The several reactions were tried through repeatedly with a pure acid prepared by the interaction of iodine and hydrogen sulfide, and also with a commercial constant boiling acid stabilized by the addition of 1-2% of hypophosphorous acid. Since the use of the stabilized acid is so much more convenient from a practical manipulative viewpoint, duplicate experiments using this mixture were performed in view of the possible applications of these reactions in chemical analysis. Qualitatively, and to a large extent quantitatively, practically no differences were observed in the behavior of the two acids except in respect to ease of air oxidation and amount of free iodine liberated in the reactions. The several sulfates used in these experiments were prepared by the writer from pure chemicals.

In the following experiments the general procedure was to treat weighed samples of the finely divided solids with definite volumes of acid of known concentration at various temperatures, noting evidences of a reaction or lack of reaction and, in the case of a reaction taking place, collecting and examining the gaseous or solid products by the usual qualitative or quantitative methods, usually both. In cases where pure hydriodic acid was employed the reactions were studied under a carbon dioxide atmosphere, while the corresponding experiments with the stabilized acid were performed in air.

Alkaline Earth Sulfates.—At room temperature the sulfates of barium, strontium and calcium are somewhat less soluble in concentrated solutions of hydriodic acid than in solutions of hydrochloric or hydrobromic acids of like normality, as found by a series of solubility determinations. On the other hand, these compounds have a much higher apparent solubility in hot solutions of concentrated hydriodic acid than in similar solutions of hydrochloric and hydrobromic acids due to an oxidation-reduction reaction progressively occurring between the dissolved salt and the acid, that results in the formation of hydrogen sulfide, iodine, water, and the corresponding metallic iodides. The onset of this reaction is dependent on acid concentration, temperature, and the sulfate-ion concentration as furnished by a particular salt, varying for the salts in the order of their solubility as shown in Table I. The following results are illustrative of the speed with which constant boiling hydriodic acid effects the decomposition of these sulfates at the boiling point in an open vessel. With the quantities given in the footnote to the table, complete decomposition of calcium sulfate occurs in about one minute, that of strontium sulfate in from seven to eight minutes, while barium sulfate decomposes only to the extent of about 60% in twenty minutes. Complete decomposition of the latter cannot be effected under these conditions due principally to the adverse effect of the progressive increase in barium-ion concentration on the solubility of

TABLE I

INFLUENCE OF ACID CONCENTRATION AND TEMPERATURE ON THRESHOLD APPEARANCE OF THE REACTION BETWEEN ALKALINE EARTH SULFATES AND HYDRIODIC ACID[a]

Effect sought	Acid normality	Barium sulfate	Strontium sulfate	Calcium sulfate
Apparent rate of decomposition in boiling acid of medium concentration	1.0	Nil	Nil	Very slow
	2.0	Nil	Very slow	Slow
	3.0	Very slow	Slow	Mod. slow
Apparent rate of decomposition in constant boiling acid at the boiling point	7.6	Slow	Mod.	Rapid
Approximate temperature of beginning reaction in constant boiling acid, °C.	7.6	85	60	50

[a] In each of these experiments a 100-mg. sample of the powdered (100-mesh) sulfate was suspended in 10 cc. of acid in a tube containing a strip of lead acetate paper suspended above the liquid. Evolution of hydrogen sulfide was used as an indication of the start of the reaction and length of paper stained in a given time an indication of the rate of decomposition.

the sulfate and hence on the concentration of dissolved salt available for further reaction. By using successive fresh portions of acid, however, small samples of barium sulfate can be transposed completely. That this decomposition is not due to a direct surface action of the hydriodic acid on these sulfates was indicated by experiments in which a soluble sulfate was first dissolved in cold constant boiling acid in an amount just sufficient to reproduce the initial concentration of sulfate ion furnished by the previously-measured slight solubility of a given alkaline earth sulfate, and then the resulting homogeneous solution was heated. Under these conditions it was observed that the action started at about the same temperature and gave the same reduction products as though the particular alkaline earth sulfate were present. The decomposition of alkaline earth sulfates by hot concentrated hydriodic acid apparently takes place then in two principal stages. First, the salts dissolve to a limited extent in the acid, furnishing the usual ions to the solution, after which the oxidation–reduction reaction takes place between the sulfate ions and the acid. The two stages follow each other progressively and the total rate of decomposition with a given salt depends primarily on the velocity with which sulfate ions are furnished to the solution, which is governed by the specific solubility of the salt, its particle size and the degree of agitation. Second, the rate is determined by the velocity of the oxidation–reduction reaction itself, which is practically imperceptible at room temperature, quite rapid at the boiling point of the acid, and dependent on both sulfate ion and hydrogen iodide concentration, the latter having been found to be of greater influence.

In formulating suitable equations to represent the decomposition of alkaline earth sulfates by hot concentrated hydriodic acid, the following facts must be considered. The essential chemical change consists in the reduction of sulfate ion by the acid with the formation of hydrogen sulfide, iodine, water, and iodide ions as the only discernible products of the primary reaction. To a limited extent secondary reactions also occur between these products, such as that between the hydrogen sulfide and the free iodine to form hydrogen iodide and free sulfur, with some oxidation of the latter, when air is present, to form sulfur dioxide. These latter reactions were found, however, to occur largely in the gas phase above the solution. This reaction has a marked temperature coefficient and a measurable rate of speed, so that it is probably not wholly ionic. Hence it seems most likely that it is largely molecular hydrogen iodide that engages in the reaction with the sulfate ion. On these bases one may write: $SO_4^{=} + 10HI \longrightarrow H_2S + 4H_2O + 4I_2 + 2I^-$. In a given case the total stoichiometric change can be represented by the equation: $SrSO_4 + 10HI \longrightarrow SrI_2 + H_2S + 4H_2O + 4I_2$.

Chromic Dihydroheptasulfate.—The peculiar compound formed by fuming a mixture of chromic hydroxide, or a soluble chromic salt, with an excess of concentrated sulfuric acid for several hours is remarkable for its high resistance to the action of nearly all acids, acid mixtures, and fused salts. Some recent writers have considered this compound to be normal anhydrous chromic sulfate in spite of the considerable evidence existing in the literature respecting its complex nature. By reason of this element of doubt, the compound prepared for use in these experiments from chromium nitrate was checked as to composition and the empirical formula $Cr_4H_2(SO_4)_7$ was again confirmed.

It has been shown by Noyes and Bray[4] that chromic dihydroheptasulfate is attacked slowly by hot concentrated hydrochloric or hydrobromic acid, the latter being more effective. Complete decomposition by these acids requires, however, an excessive number of hours even with small samples. On the other hand, hot concentrated hydriodic acid not only attacks this compound at a higher initial rate, but complete decomposition and solution can be effected in a reasonable time. By using constant boiling acid this substance is decomposed in boiling solution more rapidly than barium sulfate, but not nearly as rapidly as strontium sulfate. Apparently when chromic dihydroheptasulfate is decomposed by the action of hydrochloric or hydrobromic acid, the action involves only the slow initial breakdown of the complex, furnishing chromic and sulfate ions to the solution, and as the concentration of these increases the system tends to reach a state of equilibrium. With hot hydriodic acid, however, equilibrium is not reached due to the continuous destruction of the sulfate ions by the hydrogen iodide with the formation of hydrogen sulfide, iodine, water and iodide ions. This is believed to explain, in some measure, the greater effectiveness of this acid in decomposing the compound.

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[4] "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, 1927, pp. 315, 319.

The total stoichiometric change involved in the reaction can be represented by the equation: $Cr_4H_2(SO_4)_7 + 68HI \longrightarrow 4CrI_3 + 7H_2S + 28H_2O + 28I_2$. This equation is admittedly unusual by reason of the large coefficients before some of the quantities, but it is thought to represent the facts. It explains why, in accordance with experiment, such a large proportion of hydriodic acid is required for the complete decomposition of a given quantity of chromic dihydroheptasulfate.

Lead Sulfate.—It has long been known that an iodide solution placed in contact with lead sulfate causes the partial transformation of the latter into lead iodide, but it does not seem to have been previously observed that a comparatively small volume of cold concentrated hydriodic acid completely transforms the salt into the iodide due to the progressive solution of this in the acid with complex formation, leaving free sulfuric acid in the resulting homogeneous golden-yellow liquid. For example, it was found that at 23° only 4.00 cc. of constant boiling acid is required for the solution of 1.000 g. of lead sulfate. This effect falls off rapidly with decrease in acid concentration, so that slight or extended dilution of a solution obtained in this manner results in a copious precipitation of lead iodide.

The nature of the complex formed when hydriodic acid reacts with lead iodide was briefly investigated by Berthelot,[5] who isolated from the solution an unstable compound $PbI_2 \cdot HI \cdot 5H_2O$ which he termed lead hydriodide. This formula, however, rests on a single partial analysis, so by way of confirmation a quantity of the compound was prepared and analyzed with the following results.

Anal. Calcd. for $PbI_2 \cdot HI \cdot 5H_2O$: Pb, 30.51; I, 56.07; H_2O, 13.27. *Found:* Pb, 30.80; I, 55.66; H_2O, 13.40.

In migration experiments performed on concentrated lead iodide–hydriodic acid solutions, movement of lead to the anode was observed, indicating the existence of the metal in the negative ion. For this reason it seems probable that in such solutions the complex is largely iodoplumbous acid with the formula $HPbI_3$, assuming that it exists in solution with the same molecular ratio between constituents as in the above solid compound, which can be considered as being a hydrated form of this acid.

The total change, then, involved in the solution of lead sulfate by cold concentrated hydriodic acid can be represented by the equation: $PbSO_4 + 3HI \longrightarrow HPbI_3 + H_2SO_4$.

When a solution obtained in the above manner is heated, or when lead sulfate is treated with the hot concentrated acid, the oxidation–reduction reaction between sulfate ions and hydrogen iodide then ensues as with the other slightly soluble sulfates, except that in this case the decomposition is very rapid due to the speed with which all the possible sulfate ion becomes available for the reaction.

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(5) Berthelot, *Compt. rend.*, **91**, 1024 (1880); *Ann. chim. phys.*, [5] **23**, 85 (1881).

Applications.—The above means of decomposing difficultly soluble sulfates has been found to be of considerable practical value in analysis. For example, the presence of such sulfates in the acid insoluble residue obtained in the usual qualitative scheme can be detected readily by heating a sample of the dried residue with stabilized constant boiling acid and testing for the evolution of hydrogen sulfide by means of lead acetate paper. After proper treatment of the resulting solution, the metals can then be detected by the usual reactions. Rapid identification of natural alkaline earth sulfates can be made in this manner as shown by tests on minerals of known character. In quantitative analysis also, hydriodic acid can be used for difficult separations involving these sulfates. As a test of its value in this respect a series of experiments were made on the separation of mixtures of quartz and alkaline earth sulfates. In these analyses each mixture was boiled for a sufficient period with a small volume, or successive small volumes, of the concentrated acid, after which the unattacked silica was transferred to a filtering crucible, washed a few times with water, dried and weighed. Good quantitative separation was obtained. In general, the use of finely-divided samples is essential for the most certain and rapid analytical application of this method of decomposition, especially in dealing with barium sulfate. It is planned to work out in a more detailed manner these uses of hydriodic acid in analytical chemistry.

Summary

All the difficultly soluble sulfates can be decomposed by the action of hot concentrated hydriodic acid. The apparent mechanism involves the reduction by hydrogen iodide of the sulfate ions continuously furnished to the acid solution by these salts with the resulting formation of hydrogen sulfide, iodine, and water, leaving the corresponding metallic iodides in solution. Lead sulfate is also quite soluble in hydriodic acid of high concentration at room temperature. The value of these reactions in chemical analysis has been indicated.

PRINCETON, NEW JERSEY

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[A CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF KENTUCKY]

The Effect of Hydrogen-Ion Concentration on the Flocculation Values of Chromic and Aluminum Oxide Sols

BY M. HUME BEDFORD, W. H. KELLER AND J. L. GABBARD

Most of the previous investigations of the variation of flocculation values of hydrous oxide sols with hydrogen-ion concentration have been made in the presence of buffers and other contaminants,[1] or without a direct measure of the hydrogen-ion concentration.[2] But Hazel and Sorum[3] have devised a procedure for investigating the flocculation values of a series of hydrous oxide sols of gradually increasing and directly measured hydrogen-ion concentrations and free from any contaminating ions. This paper reports an application of their method to chromic and aluminum oxide sols.

The hydrogen-ion concentration was controlled by adding equal volumes of very dilute hydrochloric acid of slightly increasing concentrations to equal volumes of stock sols. Hydrogen-ion concentrations were measured by the use of the glass electrode and a vacuum tube voltmeter. Flocculation values were determined by adding equal volumes of the coagulating electrolyte of slightly increasing concentrations to samples of the sol until that concentration of electrolyte was found which, on standing for twenty-four hours, just produced complete coagulation.

Measurements.—Hydrogen-ion concentrations were determined potentiometrically. The glass electrode described by MacInnes and others[4] was used instead of the platinized hydrogen electrode. The glass electrode is greatly superior for this work because it is not poisoned by contaminants, does not tend to coagulate the sol or change its *P*H value during measurements, and allows practically instantaneous readings.

Each glass electrode has a characteristic "asymmetry" potential which is large (as high as several volts) just after the electrode is made, but which gradually decreases to about 0.1 volt while the electrode is "aged" by immersion in dilute hydrochloric acid for several days, and is fairly constant thereafter. This constant was determined for the electrode before and after each set of readings by the use of standard buffer solutions, as described by Hazel and Sorum.[3]

Buffers of KCl–HCl, *P*H 2.2, NaAc–HAc, *P*H 4.63, and KH_2PO_4–Na_2HPO_4, *P*H 5.9 were used. The *P*H values of the buffers were checked with a standard hydrogen electrode. The constant of the electrode checked by the buffers just before and after each set of readings always agreed to within 0.02 of a *P*H unit. The constant is calculated by the equation: $P_H = (E\text{ (cell)} + C)/0.059$ at 25°, where C is the desired constant and E is the measured e. m. f. of the cell.[5]

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(1) Harry B. Weiser and E. E. Porter, *J. Phys. Chem.*, **31**, 1383 (1927).

(2) S. Ghosh and N. R. Dhar, *idid.*, **29**, 659 (1925); **30**, 830 (1926). N. R. Dhar and V. Gore, *J. Indian Chem. Soc.*, **6**, 31 (1929), from *Chem. Abst.*, **23**, 2628 (1929).

(3) Fred Hazel and C. H. Sorum, THIS JOURNAL, **53**, 49 (1931).

(4) D. A. MacInnes and Malcolm Dole, *ibid.*, **52**, 29 (1930); D. A. MacInnes and Donald Belcher, *ibid.*, **53**, 3315 (1931).

(5) Because methods described in the literature for making glass electrodes are both meager and

The hydrogen electrode was coupled with a normal calomel electrode through a salt bridge. The e. m. f. of the completed cell was measured by a vacuum-tube voltmeter of the type described by Partridge.[6] A Leeds and Northrop Student Potentiometer was used in place of the voltmeter in the Partridge circuit.

Precipitating values were determined by adding 3 cc. of the electrolyte to 2 cc. of sol, shaking thoroughly, and permitting the mixture to stand, stoppered, for twenty-four hours. Increasing concentrations of electrolyte were prepared by adding stock electrolyte of convenient concentration (previously determined) by 0.1-cc. increments to a 3-cc. vessel, and diluting to the mark (3 cc.) with distilled water. That concentration which just produced complete coagulation in twenty-four hours was taken as the flocculation value of the sol toward that electrolyte expressed in millimoles of electrolyte per liter of mixture.

This definition of the coagulating value is entirely arbitrary and was used merely as a matter of convenience. The values obtained are only relative, but are of less than 3.33% error with respect to each other. This limit of error is due to the fact that precipitants were added in 3.33% increments of concentration. That the values are valid relatively within this limit was demonstrated experimentally by the failure of 3.33% less electrolyte to produce complete coagulation, even when the sol so treated was left standing for several days.

With univalent and bivalent anions coagulation was usually quite definite. When a perfectly colorless layer of water one millimeter or more in depth was observable above the settling precipitate, coagulation was always found to be complete. This was shown by centrifuging for fifteen minutes at 1500 to 2500 r. p. m. and testing the supernatant liquid qualitatively for the metal. The salts of trivalent cations such as ferric, chromic, and aluminum ions produced a troublesome partial sedimentation very difficult to detect visually, the coagulum even being repeptized on centrifuging. It was necessary to repeat such precipitations until a qualitative test definitely indicated complete coagulation. The aluminum oxide sol particularly produced partial sedimentations which were very difficult to distinguish from complete coagulations because of the practically colorless nature of the sol. In such instances the samples were allowed to stand longer than twenty-four hours to let the coagulum settle further so that a sufficiently large quantity of the supernatant liquid could be drawn off for examination by the aluminon test.

Preparation of Sols.—The chromic oxide sol was prepared by hydrolysis of chromic chloride with boiling distilled water[7] and hot dialysis[8] through cellophane.[9] Dialysis was conducted at 85 to 90° for about twelve to fourteen hours per day for three weeks. At the conclusion of the dialysis, when treated with silver nitrate, distilled water which had stood overnight in contact with the sol through the cellophane failed to show any trace whatever of chloride ion. A sample of the sol dissolved in hot nitric acid showed a very faint cloudiness with silver nitrate due to the chloride ion adsorbed by the micelles. The sol contained 1.35 g. of chromium per liter and its P_H value at the conclusion of dialysis was found to be 6.4.

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difficult, a new and ingenious process was devised which produced a stronger electrode and saved much time By careful suction applied by the mouth to a rubber tube attached to the electrode tube, the glass membrane is gently drawn against and fused onto the hot end of the electrode tube held just above it, thus producing an electrode which because its inner surface is convex, is consequently stronger than those with plane surfaces obtained by the methods previously described. MacInnes and Belcher suggest that only one electrode be made from each bubble, but the writers found that by the above procedure a number of electrodes could be made from the pieces of each bubble. Fairly thick (not iridescent) membranes were also found to be quite efficient.

(6) H. M. Partridge, THIS JOURNAL, 51, 1 (1929).

(7) Marks Neidle and Jacob Barab, *ibid.*, 39, 71 (1917).

(8) Marks Neidle, *ibid.*, 38, 1270 (1916).

(9) J. W. McBain and S. S. Kistler, *J. Phys. Chem.*, 35, 130 (1931).

The aluminum oxide sol was prepared by precipitation and repeptization of aluminum hydroxide from a solution of aluminum chloride[10] and was dialyzed in a Neidle dialyzer using cellophane bags. The dialysis was conducted at 70 to 90° continuously for one week. Distilled water was allowed to flow through the cellophane bag at the rate of about 1 liter per hour. The dialyzed sol did not give a test for the aluminum ion by the aluminon test, and gave only a very slight test for the chloride ion with silver nitrate. The concentration of the sol was 1.652 g. of aluminum per liter and its *PH* value at the conclusion of dialysis was 5.85.

Data and Discussion of Results.—The writers repeated the work of Hazel and Sorum on ferric oxide sols, using two different stock sols each prepared according to the procedure of Hazel and Sorum. The flocculation values obtained were lower than those of Hazel and Sorum but the trends shown by the variations of flocculation values with hydrogen-ion concentration agreed completely with their results and substantiate fully their conclusions.

Tables I and II present the coagulation values of typical electrolytes toward chromic oxide and aluminum oxide sols, respectively.

TABLE I

FLOCCULATION VALUES IN MILLIMOLES PER LITER OF CHROMIC OXIDE SOLS CONTAINING 1.35 G. OF Cr PER LITER

Sols	1	2	3	4	5
PH	5.3	4.9	4.5	4.0	3.5
Electrolyte					
KBr	5.0	8.0	16.0	30.0	...
$^1/_3AlCl_3$	600.0	600.0	600.0	640.0	No ppt.
K_2SO_4	0.136	0.16	0.24	0.32	0.56
$CaSO_4$	.112	.124	.192	.24	.48
$K_3Fe(CN)_6$	.064	.076	.12	.17	.31
$K_4Fe(CN)_6$	.044	.060	.088	.12	.30

TABLE II

FLOCCULATION VALUES IN MILLIMOLES PER LITER OF ALUMINUM OXIDE SOLS CONTAINING 1.22 G. Al PER LITER

Sol	1	2	3	4	5
PH	5.67	5.22	4.74	4.40	3.96
Electrolyte					
KCl	26.0	30.0	34.0	46.0	100.0
K_2SO_4	0.34	0.40	0.44	0.50	0.60
$K_3Fe(CN)_6$	.13	.15	.16	.18	.19
$K_4Fe(CN)_6$	.096	.108	.13	.17	.18
K_2CrO_4	.30	...	.40	..	1.04
$^1/_2BaCl_2$	32.0	...	40.0	..	80.0
$^1/_3AlCl_3$	80.0	...	..	..	100.0

The electrolytes are salts of uni-, bi-, tri-, and quadrivalent anions, since ferric, chromic and aluminum oxide sols are positive, and the anion the component of the solution most active in coagulation.

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(10) Harry B. Weiser, *J. Phys. Chem.*, **35**, 1368 (1931).

With two exceptions the stability of ferric oxide sol was found to vary directly with its hydrogen-ion concentration; in one case, the stability of ferric oxide sol toward sulfate ion decreased with increase of hydrogen-ion concentration; in the other case the flocculation values of the salts of trivalent metals, such as iron, chromium and aluminum, were constant within certain limits of *P*H values of sol samples. These results were obtained by Hazel and Sorum, and verified by the writers.

Chromic and aluminum oxide sols showed no exceptions whatever to the general rule that sol stability increases with increased hydrogen-ion concentration, within the limits investigated. However, the precipitating value of ferric chloride toward chromic oxide sol was constant from *P*H 5.3 to 4.5 but increased from *P*H 4.5 to 4.0, while at *P*H 3.5 ferric chloride failed entirely to coagulate the sol. This was probably due to the solution of the sol micelles in the quantity of acid from the hydrolysis of the salt added to the already considerable hydrogen-ion content of the sol.

The *P*H values of the sol samples after complete coagulation were also measured, but the trends shown by the results obtained were quite discordant and entirely unpredictable. These changes of *P*H values may have occurred at the time of mixing of electrolyte with the sol since the two systems were not isohydric, as was shown by comparison of the *P*H values of the electrolytes with those of the sols; or, the changes may have occurred during coagulation as a result of the processes accompanying coagulation; or, they may have resulted from both the mixing and the coagulation. Hence the *P*H values assigned to the sols may not represent the *P*H's at which coagulation occurred, but merely the original *P*H values of the sols. However, conclusions based on these data are perfectly valid regarding the stability toward electrolytes of these sols of the given *P*H values. Sufficient data were not collected during this investigation to determine the time of change of the *P*H values of the mixtures, and this problem is now being further investigated in this Laboratory.

Summary

1. The stability of chromic and aluminum oxide sols toward electrolytes has been shown to vary directly with their hydrogen-ion concentration.

2. The stability of ferric oxide sol varies directly with its hydrogen-ion concentration except toward sulfates, in which case the stability varies inversely with the hydrogen-ion concentration.

3. Ferric and aluminum chlorides have been shown to have constant precipitation values toward hydrous oxide sols, within certain limits of *P*H values, probably due to the maintenance of constant hydrogen-ion concentration by buffer action of the hydrolyzed salts.

LEXINGTON, KENTUCKY

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Separation and Determination of the Alkali Metals Using Perchloric Acid. V. Perchloric Acid and Chloroplatinic Acid in the Determination of Small Amounts of Potassium in the Presence of Large Amounts of Sodium

BY G. FREDERICK SMITH AND J. L. GRING

Introduction.—In a previous paper[1] the combined use of perchloric acid and chloroplatinic acid in the quantitative separation and determination of mixtures of sodium and potassium was shown to be superior to the customary use of either acid alone. We have now studied the conditions under which this method can be applied to the determination of 0.02 to 0.2% of potassium in sodium chloride.

Very small amounts of potassium in the presence of large amounts of sodium are usually determined by precipitation as potassium-sodium cobaltinitrite and the determination of potassium in the precipitate by the perchloric acid process. The present method involves but a single precipitation and is, therefore, much simpler and more rapid.

Solubility Relationships Governing the Process.—As has been shown previously,[1] the rate of decrease in solubility of potassium perchlorate in alcohol–water solutions with increasing proportions of alcohol is slight by comparison with the decrease in solubility of potassium chloroplatinate under the same conditions. Potassium perchlorate is quantitatively insoluble only in practically absolute alcohol. On the contrary, potassium chloroplatinate is quantitatively insoluble in 85% alcohol and an excess of the chloroplatinate ion. Sodium perchlorate is satisfactorily soluble in either absolute alcohol or any mixture of water and alcohol suitable for the quantitative separation of potassium as perchlorate or chloroplatinate.

For the separation of very small amounts of potassium from large amounts of sodium, conversion of the potassium to chloroplatinate is preferable to the formation of potassium perchlorate for numerous reasons, the most important consisting in the fact that the ratio $K_2PtCl_6/2KCl$ is larger than the ratio $KClO_4/KCl$. This is true notwithstanding the fact that potassium perchlorate can be shown to be less soluble in 97–100% alcohol–water mixtures when a sufficient excess of perchlorate ion is present for its common ion effect than is potassium chloroplatinate with excess of the chloroplatinate ion. In the method under discussion, the perchlorate ion is present in large excess as a result of the high concentrations (0.25–0.30 molal) of sodium perchlorate necessarily present. On the other hand, the process as a whole becomes practicable only in case a small excess of chloroplatinic acid is required as compared to the unmodified Fresenius method.

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[1] Smith and Shead, THIS JOURNAL, 54, 1722 (1932).

The reaction upon which the method is based is $2KClO_4$ (small amounts) + $NaClO_4$ (large amounts) + $H_2PtCl_6 \rightleftharpoons K_2PtCl_6 + NaClO_4 + 2HClO_4$. The present study consists in the determination of the maximum concentration of sodium perchlorate which may be present to complete the reaction in the sense from left to right. Partial reversal of this reaction would result in the formation of a mixed precipitate of $K_2PtCl_6 + KClO_4$, whereas only potassium chloroplatinate is desired. The reaction is affected by two remaining variables, first, the water concentration in the solvent alcohol, and second, the excess of chloroplatinic acid used as precipitant.

Materials for the Study of the Method.—The reagents used are from the same stock previously described in connection with earlier papers of this series and require therefore no further description. Sodium chloride was used in such quantities that a separate stock perhaps somewhat less pure than that previously described was used. This was prepared by the recrystallization of C. P. sodium chloride from water by the use of gaseous hydrogen chloride. A trace of potassium chloride was a possible contamination but by the application of the method the amount was shown to be barely perceptible.

Determination of Maximum Permissible Perchlorate Ion Concentration and the Influence of Alcohol Strength.—The method employed consisted in preparing solutions of anhydrous sodium perchlorate in 80–100% ethyl alcohol of variable concentrations. Potassium was added to these various solutions in small amount either by the suspension of 100–200 mg. of potassium chloroplatinate or by the addition of potassium perchlorate and a slight excess of chloroplatinic acid. The solutions and precipitates thus formed were sealed in glass tubes and rotated in a thermostat at 25° until an equilibrium was established. The tubes were then opened and the precipitates filtered, dried, and examined for any potassium perchlorate partially precipitated together with potassium chloroplatinate. The study of the precipitates was carried out in a number of ways as follows: (a) microscopic examination. Suitable for extensive contamination of potassium chloroplatinate by potassium perchlorate. (b) Determination of platinum in the potassium chloroplatinate to prove the presence or absence of potassium perchlorate. (c) By the color of the solutions produced by the addition of potassium chloroplatinate to the alcoholic sodium perchlorate after equilibrium. Precipitation of potassium perchlorate resulted in the formation of chloroplatinic acid in solution, identified by its color. (d) By adding weighed amounts of potassium chloroplatinate and testing for quantitative recovery.

The data thus obtained defined the maximum concentration of sodium perchlorate which may be present without the formation of potassium perchlorate. The data are presented graphically in the accompanying Fig. 1. But a slight excess of chloroplatinic acid was employed in these experiments since in actual practice larger excesses would make the results more selective in the proper sense due to the decreased solubilities of potassium chloroplatinate.

Analytical Interpretation of the Experimental Results.—The study of the data of Fig. 1 leads to the following conclusions. (1) The maximum concentration of sodium perchlorate which may be present is 0.28 molal using 95% alcohol. (2) 80–90% alcohol permits the presence of a constant concentration of sodium perchlorate, 0.20 molal. (3) Using 95–100% alcohol, the precipitation of potassium perchlorate takes place to the exclusion of potassium chloroplatinate with rapidly decreasing concentrations of sodium perchlorate. (4) For each 100 cc. of 95% alcohol, 1.63 g. of sodium chloride can be used as sample for analysis. (5) Since potassium perchlorate is known to become increasingly less soluble in more concentrated alcohol, these data show that 95% ethyl alcohol causes the least dissociation of sodium perchlorate. Since 95% ethyl alcohol is the most commonly occurring strength, this fact is a fortunate circumstance operating to simplify the process.

Outline of Procedure.—1.48 to 1.63 g. of sodium chloride (containing potassium chloride) sufficient to give a sodium concentration of 0.25–0.28 normal is dissolved in water in a 150-cc. beaker and converted to sodium and potassium perchlorate using twice the perchloric acid required. The residue thus obtained is freed from excess perchloric acid by heating, the last part of the operation being carried out on a wire gauze over a free flame, the beaker being rotated with the cover glass supported on glass hooks and the beaker walls brushed carefully by the flame to remove perchloric acid condensed on the inside walls of the beaker and under side of the cover glass. If evaporation of the sodium perchlorate solution has been carried out above 35°, the residue is anhydrous upon deposition from the water–perchloric acid solution.

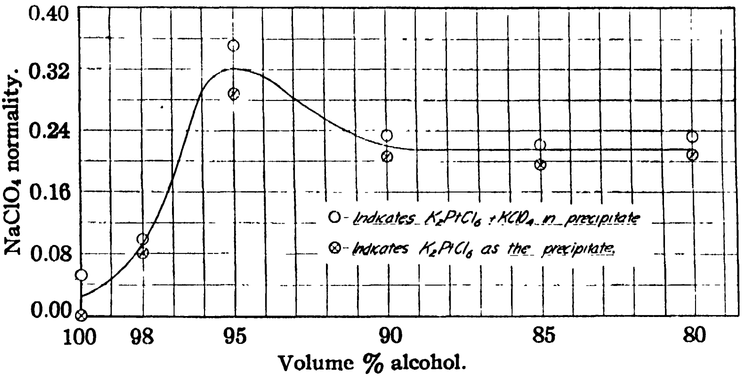

Fig. 1.—Selective precipitation of K_2PtCl_6 from $KClO_4$ and $NaClO_4$ solutions: influence of alcohol strength.

The beaker is cooled, the inside rinsed with a few ml. of water, and the evaporation and heating repeated for the second time. By this operation the perchloric acid occluded in the first obtained anhydrous sodium perchlorate is freed and the residue is acid free. Dissolve the salts by adding 95 ml. of 95% ethyl alcohol and heating if desired up to near the boiling point on the hot-plate. (The heating of such solutions is perfectly safe since free acid is not present.) Chloroplatinic acid, 0.2 g. in 5 ml. of 95% ethyl alcohol, is added to this solution, preferably hot, and after a few minutes' digestion and vigorous stirring the mixture is cooled to 0° and allowed to stand with frequent stirring at this temperature for an hour or longer.

The precipitated solution is filtered through a sintered glass or quartz filtering crucible, the potassium chloroplatinate washed once with 95% alcohol and finally with cold absolute alcohol until free from sodium perchlorate (9–10 portions of 1 ml. each) and finally dried and weighed. The potassium chloroplatinate is stable at 350° and its weight may be checked by solution in hot water and precipitation of the platinum by acidification with hydrochloric acid and decomposition with a few milligrams of magnesium ribbon. The precipitated platinum is then filtered on a small ashless filter which is dried, ignited and weighed, from which value the amount of potassium chloride originally present is calculated using the theoretical factor.

Experimental Analyses.—The first variable requiring study was the determination of the required excess of chloroplatinate ion. Weighed amounts of sodium chloride were treated with weighed amounts of potassium chloride in the form of a dilute solution in water using a weight buret to increase the accuracy of obtaining the small amounts of potassium chloride. Solutions were prepared for analysis as above described and various weights of chloroplatinic acid were added and the effects determined. The results of these analyses are given in Table I. Precipitations were carried out in 100 cc. of 95% alcohol.

TABLE I

THE INFLUENCE OF EXCESS CHLOROPLATINIC ACID ON THE SEPARATION OF SMALL AMOUNTS OF POTASSIUM IN THE PRESENCE OF LARGE AMOUNTS OF SODIUM

KCl, g.	NaCl, g.	Excess $H_2PtCl_6 \cdot 6H_2O$, g.	$NaClO_4$, normality	K_2PtCl_6 found, g.	KCl calcd., %	KCl found, %	Error KCl unpptd., %
0.0010	1.4705	0.0025	0.25	0.0003	0.068	0.006	90
.0020	1.4600	.0038	.25	.0011	.137	.019	83
.0039	1.4225	.0096	.24	.0061	.266	.131	58
.0012	1.4281	.0680	.24	.0028	.084	.052	38
.0024	1.4724	.1000	.25	.0071	.163	.148	9

Results from Table I indicate that an excess of somewhat greater than 100 mg. of $H_2PtCl_6 \cdot 6H_2O$ in 100 ml. of solution should provide a sufficient excess of precipitant; 200 mg. of precipitant per 100 ml. of solution was therefore chosen as a safe working basis. Results obtained in final tests of the new method of analysis are given in Table II.

TABLE II

THE SEPARATION OF SMALL AMOUNTS OF POTASSIUM IN PRESENCE OF LARGE AMOUNTS OF SODIUM

Volume of solution precipitated, 100 ml. Acid used, 0.20 g. of $H_2PtCl_6 \cdot 6H_2O$ per determination. Temperature of precipitation, 0°.

KCl, g.	NaCl, g.	$NaClO_4$ normality	K_2PtCl_6 calcd., g.	K_2PtCl_6 found, g.	Pt found, g.	Pt calcd., g.	KCl found, g.	KCl found, %.	Error KCl, g.
0.0021	1.4483	0.244	0.0069	0.0073	0.0029	0.0029	0.0022	0.152	+0.0001
.0020	1.4598	.25	.0065	.0068	.0027	.0026	.0021	.142	+ .0001
.0021	1.3888	.235	.0069	.0073	.0029	.0029	.0022	.153	+ .0001
.0019	1.4394	.243	.0063	.0069	...	...	.0021	.145	+ .0002
Blank	1.48	.25	...	.0006	...	...	.00018	.012	....

From an examination of Table II it is seen that 0.15% of potassium chloride in sodium chloride can be determined readily by one precipitation with an accuracy of 5% if the blank correction for the determination of the trace of potassium in the sodium chloride used to test the results is disregarded. Applying the blank correction, the results obtained are as accurate as are those obtained in analyses of the ordinary rather than the semi-micro type. While the analyses of Table II deal with comparatively large amounts of potassium chloride, the method has been applied with equal success to much smaller amounts of potassium approaching that of the blank determination given above. The method has already been shown to apply admirably to large amounts of potassium[1] and by examination of the last table of results in that paper, it will be seen that in the cases in which the method did not apply for small amounts the cause is found in either the use of too high concentrations of sodium salts or the incorrect strength of solvent alcohol. If the directions are properly followed, no free perchloric acid is left, and so there is no danger in heating the alcoholic solutions.

Summary

1. The method of Smith and Shead[1] has been extended to include the determination of small quantities of potassium in the presence of large amounts of sodium.

2. The salts of sodium and potassium, in the modified procedure, are converted to the neutral anhydrous perchlorates, dissolved in 95% alcohol, and treated with a moderate excess of chloroplatinic acid. The precipitate of potassium chloroplatinate can be weighed as such, or converted to platinum and the potassium calculated from this.

3. The method involves the direct precipitation of potassium (one operation) and no previous concentration to isolate the potassium for subsequent purification is required.

4. The method involves the use of but 0.20 g. of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) per determination. The demand for, and cost of recovery of, platinum is therefore a small factor.

5. In analyses of samples of sodium chloride containing no more than 0.15% of potassium chloride, results obtained by the method should not be in error by more than 0.01%.

URBANA, ILLINOIS

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The Systems (a) Ammonium *d*-Tartrate–Lithium *d*-Tartrate–Water, and (b) Ammonium Lithium *d*-Tartrate–Ammonium Lithium *l*-Tartrate–Water

BY ALAN NEWTON CAMPBELL AND LOUIS SLOTIN

Pasteur's first method of resolution of optically active substances has so far only been found applicable to a relatively few cases, the reason being that most inactive forms at room temperature are true racemates and not conglomerates. A study of the mixed solubilities will always tell whether or not the transition point lies in an attainable region. Such studies have been carried out by van't Hoff and by Findlay. So far as is known to the present authors, the only racemic salts whose transition points are known are sodium ammonium racemate,[1] sodium potassium racemate,[2] and rubidium racemate.[3]

It was thought therefore that it would be of interest to investigate the effect on the transition temperature of the substitution of lithium for so-

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(1) Van't Hoff and van Deventer, *Z. physik. Chem.*, **1**, 165 (1887).

(2) Van't Hoff, *ibid.*, **17**, 505.

(3) Van't Hoff and Muller, *Ber.*, **31**, 2206 (1898).

dium in sodium ammonium racemate. Such a study as this should, for completeness, comprise five systems, namely

NH_4 *d*-tartrate–Li *d*-tartrate–H_2O (1)
NH_4 *d*-tartrate–NH_4 *l*-tartrate–H_2O (2)
Li *d*-tartrate–Li *l*-tartrate–H_2O (3)
NH_4 *r*-tartrate–Li *r*-tartrate–H_2O (4)
NH_4Li *d*-tartrate–NH_4Li *l*-tartrate–H_2O (5)

Only with this complete knowledge can one be certain that system 5, on which interest centers, is really a three-component system. Only systems 1 and 5 were investigated by us, but it will be seen from an examination of the isotherms that we were justified in assuming that none of the components of system 5 broke into single constituents at the temperature of investigation.

Experimental

All the salts used in this investigation had previously been prepared. The information attainable in the literature is summarized in the table.

Salt	Prepared by	Formula assigned	Solubility in H_2O
NH_4 *d*-tartrate	Scacchi[a]	$(NH_4)_2C_4H_4O_6$	Unknown
Li *d*-tartrate	Dulk[b]	......	Readily soluble
NH_4Li *d*-tartrate	Scacchi[a]	$Li(NH_4)C_4H_4O_6 \cdot 0.5$ or $1H_2O$	14.186 g. per 100 g. soln. at 20°
NH_4Li *r*-tartrate	Scacchi[c]	$Li(NH_4)C_4H_4O_6 \cdot 0.5$ or $1H_2O$	13.104 g. per 100 g. soln. at 20°

[a] *Atti accad. Sci. Fis. Mat.* (*Napoli*), 3, No. 5 (1866); 6, No. 25 (1867); No. 29, pp. 29, 33 and 38.

[b] *Ann. chim. phys.*, [3] 5, 370.

[c] Scacchi, *Atti accad. Sci. Fis. Mat.* (*Napoli*), No. 5, 3 (1866), and No. 25, 29 (1867).

Ammonium *d*-tartrate was prepared by the complete neutralization of Mallinckrodt C. P. tartaric acid with ammonia. The evaporation must be conducted in the presence of excess ammonia to prevent formation of the acid salt. The salt was recrystallized twice from water. A solution of the final preparation was neutral to litmus and had $[\alpha]^{30}_D$ +34.320°. Landolt[4] gives $[\alpha]^{20}_D$ 34.260°. NH_4 found by the distillation method, 19.58%; formula requires 19.59%.

Lithium *d*-tartrate was prepared by neutralizing C. P. tartaric acid with C. P. lithium carbonate until the solution was just alkaline to phenolphthalein. The crystallized salt was purified twice by recrystallization from water. It had $[\alpha]^{30}_D$ 35.87°. Landolt[4] gives $[\alpha]^{20}_D$ 35.84°. The lithium content was determined by ignition and conversion of the residual carbonate to sulfate.[5] Li found, 9.36%; formula requires 9.38%. This method of analysis was checked, since it was the method used throughout the solubility work, by precipitation of silver tartrate. In this way, for example, the following figures were obtained: weight of lithium tartrate, 1.3423 g.; weight of lithium tartrate calculated from weight of silver, 1.3425 g. Hence the above method is satisfactory for determining lithium.

Ammonium lithium *d*-tartrate was prepared by evaporation of an equimolar solution of ammonium and lithium tartrates and was purified by recrystallization from water.

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(4) Landolt, *Ber.*, 6, 1676.

(5) Scott, "Standard Methods of Chemical Analysis," p. 414.

The purity of the salt was checked by analyzing weighed amounts and calculating from the formula the corresponding weight of double salt; thus, for example, (a) weight double salt, 3.421 g.; weight double salt from NH_4 determination, 3.4213 g.; (b) weight double salt, 1.6731 g.; weight double salt from Li determination, 1.6735 g.

For the inactive double salt, racemic acid was prepared by a method given elsewhere.[6] From this the double salt was prepared in the same way as the active double salt. The analytical figures were: (a) weight double salt, 1.6431 g.; weight double salt calculated from NH_4 determination, 1.6436 g.; (b) weight double salt, 2.0033 g.; weight double salt calculated from Li determination, 2.0029 g. The formula of the anhydrous double salt is therefore $(NH_4)_2C_4H_4O_6 \cdot Li_2C_4H_4O_6$.

All solubilities at temperatures higher than room temperature were determined by analyzing solutions obtained by stirring for a minimum of ten hours in contact with the appropriate solid phase, in an electrically heated and controlled thermostat. For this thermostat the temperature variations did not exceed 0.01°. At 0° the temperature was maintained constant by the use of ice and here the temperature variations amounted to 0.1°. For temperatures between 0° and room temperature, the arrangement of Walton and Judd[7] was adopted. It was found advantageous to couple this arrangement with an electrical heating unit, so that the bath was alternately heated by the heater or cooled by an entering stream of water. All thermometers were compared with a standard thermometer.

For accurate solubility work, especially where the wet solid phase is being analyzed, it is indispensable that filtration should be carried out actually in the thermostat. Accordingly, the following filtration apparatus, a modification of the previous one,[8] was used. Its construction is shown in the diagram.

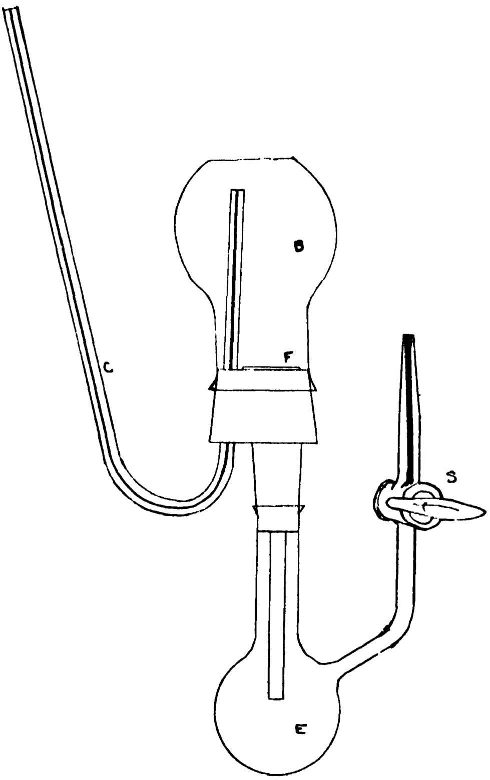

Fig. 1.

B is the bottle in which the saturated solution is prepared, F a sintered glass filter, C a capillary tube communicating with the atmosphere to equalize the pressure, E the receiver; the side-arm is for the purpose of applying suction. To operate the apparatus, the stirring apparatus is removed from the solubility bottle and the filtration apparatus and receiver inserted in its place. The whole unit is then inverted in the thermostat and the flask E slightly evacuated with a water pump. The stopcock S is then closed. The difference in pressure in the two flasks is sufficient to cause a rapid filtration of the saturated solution, the solid phase remaining on the surface of the stopper. The

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(6) Campbell, Slotin and Johnston, THIS JOURNAL, 55, 2604 (1933).

(7) Walton and Judd, *J. Phys. Chem.*, 18, 717 (1914).

(8) Campbell, *J. Chem. Soc.*, 181 (1930).

amount of evaporation from the solution during the evacuation of the lower flask is negligible, since the greater part of the liquid is in the upper part of the apparatus, and the evacuation is only carried on for a few seconds before the stopcock is closed. This method has the further advantage that no volumetric apparatus is required, both solutions and solid phase being weighed.

Solutions and solid phase were analyzed for ammonia by the distillation method, and for lithium by the method previously described. The polarimetric method was found to be insufficiently accurate for system 1, probably because of the high concentration of active material. Its use was unavoidable in system 5, where both active and inactive double salts were present, and here it seems to have been fairly accurate, possibly because no interaction is possible between the active and inactive material.

These results are expressed graphically on rectangular coördinates in Fig. 2.

TABLE I

SOLUBILITIES OF LI *d*-TARTRATE AND NH_4 *d*-TARTRATE IN THE PRESENCE OF EACH OTHER

Solubility, g./100 g. H_2O $(NH_4)_2T$	Solubility, g./100 g. H_2O Li_2T	Liquid phase $\%(NH_4)_2T$	Liquid phase $\% Li_2T$	Composition of wet residue $\%(NH_4)_2T$	Composition of wet residue $\% Li_2T$
		Temperature, 0°			
0.0	42.106	0.0	29.62	...	...
2.510	36.857	1.80	26.44	0.67	61.61
3.473	32.561	2.55	23.93	0.92	64.40
6.013	30.160	4.42	22.15	13.44	54.80
8.022	22.125	6.20	17.00	39.51	38.05
14.491	14.092	11.27	10.95	35.22	30.03
23.081	8.846	19.00	6.21	44.76	36.89
36.610	7.011	25.49	4.88	40.85	27.50
43.916	0.0	30.51	0.0	...	...
44.251	1.973	30.26	1.35	78.00	0.25
45.125	3.952	30.27	2.65	72.21	0.95
45.930	6.026	30.28	3.96	65.21	12.31
		Temperature, 30°			
Solubility, g./100 g. H_2O $(NH_4)_2T$	Solubility, g./100 g. H_2O Li_2T	Liquid phase $\%(NH_4)_2T$	Liquid phase $\% Li_2T$	Solid phase $\%(NH_4)_2T$	Solid phase $\% Li_2T$
0.0	26.661	0.0	21.05	...	...
3.076	27.143	2.36	20.84	0.20	70.93
7.703	29.181	5.63	21.32	2.34	77.88
8.337	30.001	6.37	21.62	3.17	66.20
9.350	30.661	6.68	21.90	1.05	79.71
12.764	28.561	9.03	20.21	33.49	35.32
11.980	32.731	8.28	22.62	11.56	63.47
14.672	26.071	10.43	18.53	37.29	36.40
16.744	22.603	12.02	16.22	40.31	37.20
24.662	14.732	17.70	10.57	39.16	33.50
29.651	11.603	20.99	8.22	42.31	34.15
39.671	8.182	26.83	5.53	46.24	35.17
63.600	6.916	37.29	4.06	45.60	26.73
63.813	0.0	38.95	0.0	...	...
66.205	6.771	38.30	3.92	76.20	12.82
66.310	5.326	38.64	3.11	79.60	1.13
66.871	2.102	38.73	1.12	84.47	0.98

TABLE I (*Concluded*)

Temperature, 60°

Solubility, g./100 g. H_2O		Liquid phase		Solid phase	
$(NH_4)_2T$	Li_2T	% $(NH_4)_2T$	% Li_2T	% $(NH_4)_2T$	% Li_2T
0.0	29.522	0.0	22.80	...	...
5.110	14.211	31.33	8.54	46.51	35.52
5.807	30.051	4.27	22.12	1.56	73.00
11.003	31.452	7.72	22.08	2.10	76.94
16.349	34.242	10.86	22.74	3.02	78.97
19.510	35.912	12.55	23.11	4.31	74.44
23.121	37.981	14.35	23.58	19.03	63.00
24.431	27.609	16.07	18.16	40.16	37.41
33.521	20.001	21.84	13.03	44.21	38.01
41.083	16.151	26.13	10.28	47.82	40.42
55.823	13.781	32.92	8.13	45.85	33.10
63.011	13.103	35.78	7.44	48.30	35.98
87.171	0.0	46.56	0.0	...	...
90.247	3.631	46.55	1.89	78.73	0.82
92.943	10.510	45.68	5.17	50.79	36.74
92.832	6.650	46.51	3.33	83.10	1.13
98.392	10.244	47.16	4.91	69.08	13.12

From these diagrams it appears that the transition temperature below which the active double salt cannot exist lies below room temperature. An anomaly is caused, however, by the lithium tartrate curve changing direction, an anomaly due to lithium tartrate changing its hydration, and this renders the interpretation of the curve by mere inspection difficult.

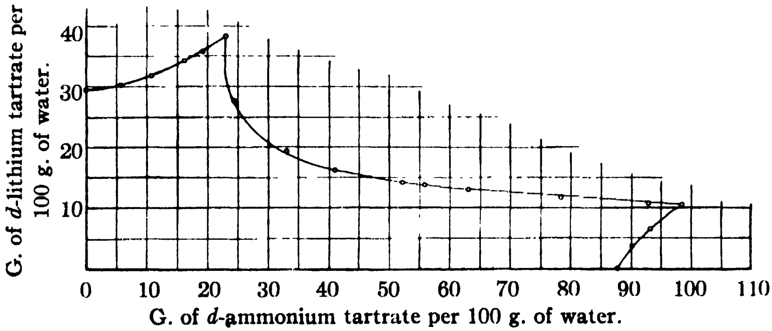

Fig. 2.—60°.

The complete triangular diagrams are given in Fig. 3.

The triangular diagram shows that the double salt has the formula $Li_2C_4H_4O_6 \cdot (NH_4)_2C_4H_4O_6$, and that it is anhydrous at all temperatures studied, although Schlossberg[9] gives to the doubled molecule 1 or $2H_2O$. The 0° triangular diagram shows that the solid phase along the lithium tartrate branch is $Li_2C_4H_4O_6 \cdot 2H_2O$, while at the higher temperatures this

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(9) Schlossberg, *Ber.*, **33**, 1084 (1900).

salt is anhydrous. The numerical value of the solubility also indicates this, lithium tartrate being more soluble at 0° than it is at 30 and 60°.

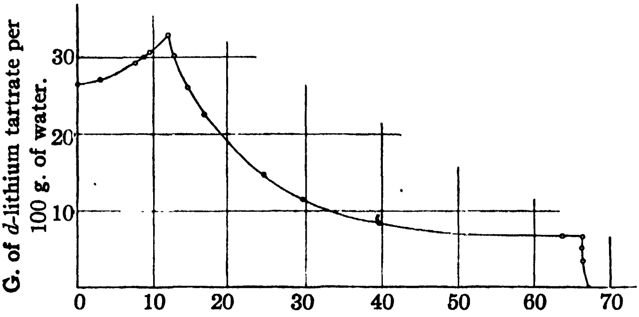

Fig. 3.—30°.

No reference to the hydration of lithium tartrate could be found in the literature, and it became advisable to determine the transition temperature of lithium tartrate dihydrate to anhydrous lithium tartrate. The dilatometric method and the solubility method were employed. By the former method the transition temperature resulted as 21.52°. The solubility figures are given in Table II.

TABLE II

SOLUBILITY OF Li *d*-TARTRATE IN WATER

Temp., °C....	60.0	45.0	30.0	25.0	20.0	10.55	8.0	0.0
Lithium tartrate per 100 g. of water, g.	29.522	27.510	26.663	26.711	27.052	31.495	33.451	42.106

When these figures are plotted against temperature, a marked point of inflection occurs at a temperature of 21.81°. Averaging the two results, the mean transition temperature for $Li_2C_4H_4O_6 \cdot 2H_2O \longrightarrow Li_2C_4H_4O_6 + 2H_2O$ results as 21.67°.

Solid Model.—In order to construct a solid model of the system, NH_4 *d*-tartrate–Li *d*-tartrate–H_2O, showing the behavior of the system with respect to temperature, it was also necessary to know the solubility curve of ammonium tartrate, since the solubility curves of the two simple salts form the boundaries of the model. The solubilities of ammonium tartrate were therefore determined and are expressed in Table III.

TABLE III

SOLUBILITY OF AMMONIUM TARTRATE

Temp., °C.	0.0	15.0	30.0	45.0	60.0
Ammonium tartrate per 100 g. of water, g.	43.916	58.101	63.813	79.450	87.171

An inspection of the solid model (not shown) reveals that the area representing stable existence of the double salt widens as the temperature increases, indicating that the double salt is more stable at higher than at lower temperatures.

At all temperatures between 0 and 60°, double salt formation takes place. In this temperature interval (a) ammonium tartrate is anhydrous; (b) lithium tartrate possesses two molecules of water of crystallization, which it loses at 21.67°; (c) the double salt is anhydrous. A rough extrapolation of the boundary lines of the area of stable existence of the double salt gives the transition temperature of $(NH_4)_2C_4H_4O_6\cdot Li_2C_4H_4O_6 \rightleftharpoons (NH_4)_2C_4H_4O_6 + Li_2C_4H_4O_6$ as −80°. An examination of the triangular diagrams also shows that the temperature interval investigated is outside of the transition interval, that is, that the double salt can be recrystallized from water without partial decomposition.

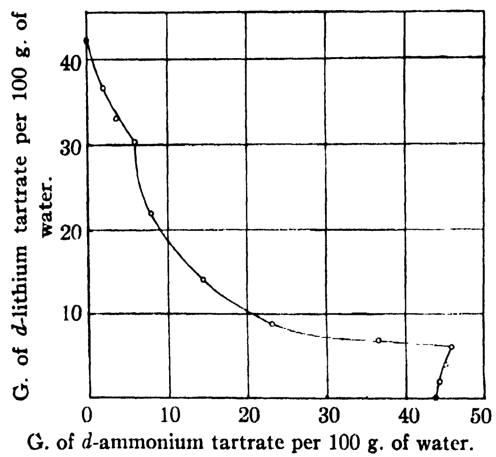

Fig. 4.—0°.

The System NH_4 Li *d*-Tartrate–NH_4 Li *l*-Tartrate–H_2O

The solubility of the inactive double salt was first determined by Schlossberg[9] who states that at 20° 100 g. of solution contains 13.104 g. of salt.

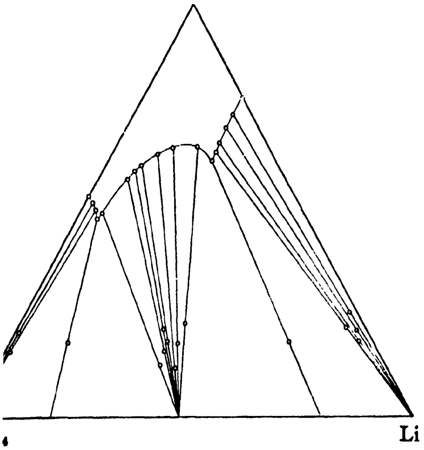

Fig. 5.—60° isothermal.

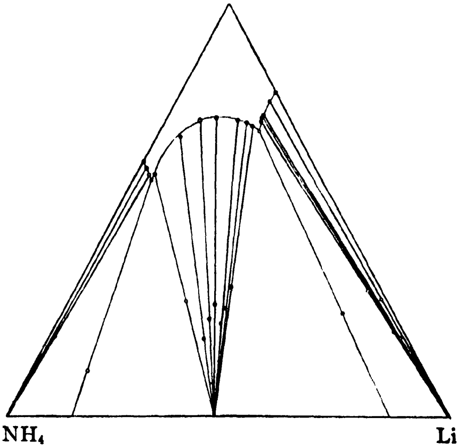

Fig. 6.—30° isothermal.

This solubility is much higher than that which was obtained in this work. It is possible that Schlossberg's double salt contained some ammonium lithium mesotartrate, which is much more soluble than the corresponding salt of racemic acid. Schlossberg's figure for the solubility of the active double salt (14.186 g. per 100 g. of solution at 20°) is considerably lower than ours.

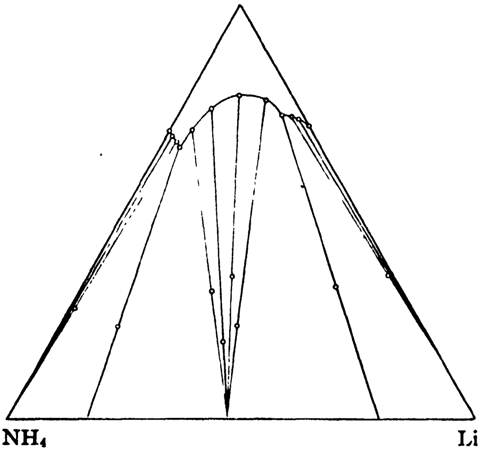

Fig. 7.—0° isothermal.

The experimental technique was the same as that of the previous system, except that the solutions and solid phases containing both active and inactive salt had to be analyzed polarimetrically. For this purpose it was necessary to determine the rotation of solutions of pure NH$_4$-Li *d*-tartrate at different concentrations. This was done for the sodium D line and at a controlled temperature of 30°, although it was subsequently found that the temperature coefficient of rotation for small changes of temperature is quite negligible. For experimental purposes, it was found simplest merely to plot observed rotation against the salt content of the solution, but for comparison with the literature, the figures are given as specific rotations.

Table IV

Specific Rotations of Solutions of NH$_4$Li *d*-Tartrate at 30° and for Na Light

Concn. in g. per 100 cc. of soln.	4.00	12.00	16.00	20.00	28.00
Concn. in g. per 100 g. of H$_2$O	4.0829	12.7480	17.4080	22.3791	32.7772
$[\alpha]^{30}_{D}$	+33.0°	+32.1°	+31.3°	+31.4°	+31.2°

Since the object of this study was merely to find the transition temperature of NH$_4$Li *r*-tartrate to its active component, the 30 and 60° isotherms were not investigated in full, but only the three invariant points were determined. Such "stability curves" are hypothetical as to their curvature, but they are sufficient to define the boundaries of the area of stable

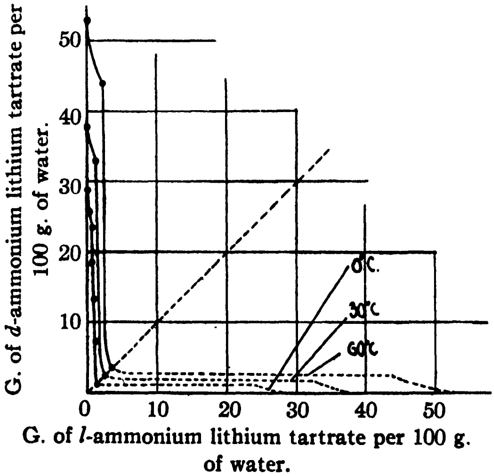

Fig. 8.

existence of the racemate. At 0°, however, the isothermal was fully investigated, in order to determine the degree of hydration of the inactive double salt. The complete data are given in Table V.

TABLE V

Solid phase	Solubility in g. per 100 g. of H_2O 0°	30°	60°
d-	28.519	37.910	52.743
r- (total *d* + *l*)	2.806	6.542	11.480
d + *r*	*d* 23.250	*d* 32.917	*d* 44.103
	l 0.731	*l* 1.416	*l* 2.312

ISOTHERMAL 0°C.

Solubilities expressed as grams of salt per 100 g. of water and also as percentages

Liquid phase: Solubility in g./100 g. of H_2O, *d*-form	*r*-form	Percentages *d*-form	*r*-form	Solid phase: Percentages *d*-form	*r*-form
0.0	2.806	0.0	2.19	...	...
6.531	2.363	6.00	2.17	2.52	74.20
12.241	1.860	10.72	1.63	3.35	67.50
17.690	1.64	14.75	1.37	6.30	56.02
23.251	1.462	18.69	1.18	45.09	29.86
24.810	0.98	19.80	0.70	76.19	0.62
28.519	.0	22.19	.0	...	...

All racemic solubilities when plotted were divided in two and one-half added to the solubility of the *d*-form, and the other half plotted as total *l*-form.

The results are plotted on rectangular coördinates in Fig. 5, and the 0° isothermal on a triangular diagram in Fig. 6.

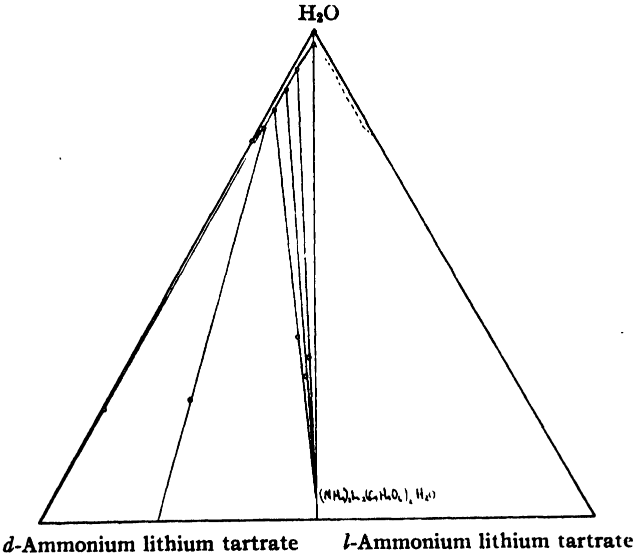

Fig. 9.—Isothermal at 0°.

The large intermediate portion of the rectangular graphs shows the racemate to be very stable at the temperatures investigated and that the transition point is well below 0°. When the solubilities of the inactive salt alone and of inactive salt plus active are plotted against temperature, the curves are found to intersect at a temperature of $-62°$. Consequently, if a solution of ammonium lithium racemate were allowed to crystallize below this temperature, it would deposit the two enantiomers. This is, of course, experimentally impossible owing to the solidification of the solvent.

The angle of intersection of the solubility curves for racemic and racemic plus active forms is large, indicating a large heat of formation.

The intersection of the double salt tie-lines on the 0° isothermal indicates for the inactive double salt the formula $(NH_4)_2Li_2(C_4H_4O_6)_2 \cdot H_2O$. This is in agreement with the findings of Scacchi and Schlossberg.[9] The hydrate also exists at 30° and quite possibly at 60°, although complete solubility measurements were not carried out to confirm this.

Summary

1. The solubility relations in the ternary systems ammonium *d*-tartrate–lithium *d*-tartrate–water and ammonium lithium *d*-tartrate–ammonium lithium *l*-tartrate–water have been determined at 0, 30 and 60°.

2. A double salt was found to be formed at all three temperatures, and its composition was established as $(NH_4)_2Li_2(C_4H_4O_6)_2$. The double salt is stable at all temperatures from 0 to 60°, becoming more stable as the temperature is raised. In the latter system a true racemate was found to exist at all three temperatures and its formula was established as $(NH_4)_2Li_2(C_4H_4O_6)_2 \cdot H_2O$.

WINNIPEG, CANADA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

The Ammines of Chromous Chloride

BY H. I. SCHLESINGER AND EDITH S. HAMMOND[1]

Chromous ammines were first prepared by Peters[2] by the action of gaseous ammonia on chromous chloride. His results were later partially verified by Ephraim,[3] who measured vapor tensions of the compounds at various temperatures. Although both investigators report the existence of a hexammine and a triammine, neither of them succeeded in causing the chromous chloride to add quite six moles of ammonia to one of the simple salt and they do not agree in their description of the color of the product. Furthermore, withdrawal of ammonia to form the triammine from the hexammine was not accompanied by an abrupt drop in the pressure as should have been the case had the measured tensions corresponded to equilibrium conditions.

Our preliminary experiments gave evidence of the existence of a pentammine and a diammine in addition to the compounds mentioned above, and showed that reinvestigation of the others was necessary to prove their existence definitely and to define their properties accurately. It very soon became obvious that the causes of the difficulty in the earlier work lay in the failure to use sufficiently purified samples of chromous chloride and to recognize the slowness with which equilibrium is attained.

Preparation of Chromous Chloride.—Chromous chloride was prepared by reducing chromic chloride with hydrogen at a furnace controlled temperature near 420°. The hydrogen was purified by passing it over hot platinized asbestos, then through a liquid air trap, followed by a phosphorus pentoxide tube, which had been evacuated and washed several times with hydrogen. The samples of chromic chloride used as starting material in the preliminary experiments were obtained by drying anhydrous chromic chloride in a stream of chlorine; for the final results, chromic chloride was resublimed in an atmosphere of pure chlorine before it was reduced. The chief difficulty is the prevention of secondary reduction of chromous chloride to chromium. The addition of hydrogen chloride to the hydrogen affords some protection against over reduction, but even under these conditions careful control of the temperature, and interruption of the reduction as soon as the color becomes pure white, are necessary. The chromous chloride thus obtained was transferred in an atmosphere of dry nitrogen to the reaction vessels in which it could be sealed, weighed and stored.

Preparation of Hexammine-Chromous Chloride.—The typical reaction vessel consisted of a glass tube about 14 × 200 millimeters, expanded at the lower end to a small flat bulb in which the chromous chloride could be spread over a fairly large area. The upper end was sealed after the chromous chloride had been introduced. Near the top was attached a side tube and stopcock through which the vessel was connected to a vacuum apparatus in which the ammonia pressure, as well as the volume of ammonia absorbed, could be measured.

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[1] This paper is taken from a thesis submitted by Edith S. Hammond to the Faculty of the Division of the Physical Sciences of the University of Chicago in part fulfilment of the requirements of the degree of Doctor of Philosophy. A part of the experimental work was carried out at the Oklahoma College for Women.

[2] Peters, *Ber.*, **42**, 4833 (1909).

[3] Ephraim, *ibid.*, **50**, 535 (1917).

After the tube containing chromous chloride was evacuated and weighed, pure dry ammonia at approximately 75 cm. pressure was admitted to the vessel. Absorption began at once with evolution of heat. To make certain that the reaction was complete, weighings were made only after the material showed no absorption for a period of about twenty-four hours. By deducting from the gain in weight of the vessel the weight of ammonia remaining in the gas phase, the amount of ammonia absorbed by the solid was obtained. In several experiments this weight was checked by measuring the volume of ammonia absorbed, but the gravimetric measurements proved more reliable. The data are reproduced in Table I.

TABLE I

COMPOSITION IN THE SYSTEM OF HEXAMMINE–CHROMOUS CHLORIDE

Sample number	Mole of chromous chloride	Approximate temperature, °C.	Final ammonia pressure, cm.	Ammonia absorbed, mole	Moles of ammonia per mole of $CrCl_2$
1	0.003448	27	46.35	0.02021	5.86
1	.003448	27	88.2	.02044	5.92
11	.001965	27	72.2	.01161	5.97
7	.001346	23	30.82	.00787	5.85
7	.001346	26	76.14	.00797	5.92
7	.001346	23	105.15	.00808	6.00
9	.001735	23	30.37	.01018	5.87
9	.001735	23	79.25	.01025	5.91
9	.001735	23	100.09	.01040	5.99
6	.001074	20	134.38	.00659	0.613
6	.001074	20	99.4	.00658	6.125
6	.001074	20	74.28	.006565	6.11
6	.001074	20	29.33	.00636	5.92
6	.001074	20	24.72	.00635	5.91
6	.001074	20	21.09	.00635	5.91
4	.001286	23	105.08	.00815	6.34
4	.001286	23	73.25	.00788	6.13
4	.001286	23	40.77	.00777	6.04
4	.001286	26	31.16	.00771	6.00
4	.001286	24	21.14	.00771	6.00

The table shows clearly the importance of using only the purest possible chromous chloride in experiments of this type. The data obtained with samples 1, 7, 9 and 11 which were made from unsublimed chromic chloride, while consistent among themselves, lead to the incorrect conclusion that absorption of six moles of ammonia does not occur until the pressure is near 100 cm. The more nearly pure the sample of chromous chloride, the lower the pressure required for the absorption of ammonia, as is seen from the experiment with sample No. 6 in which 5.91 moles of ammonia are taken up at pressures between 21 and 29 cm. The amount of ammonia absorbed by the most carefully purified sample (No. 4) is that required for the hexammine, and remains constant in a pressure range from about 20 to between 30 and 35 cm. At pressures below 18 cm., ammonia is again lost and the color changes from deep blue to violet. These pressure values, however, represent merely convenient criteria for the preparation of the hexammine; the determination of the equilibrium pressures and definite evidence for the existence of the hexammine are described below.

Before turning to these measurements, a word should be said about the phenomena which accompany increase of the ammonia pressure beyond the limits mentioned above. At higher pressures the material becomes green, and when the pressure reaches 90 cm., gray. During these color changes small amounts of ammonia are absorbed very slowly; but even though the pressure is raised to 2 atmospheres and the temperature lowered to −15°, the maximum absorption corresponds to only 0.34 mole of ammonia in excess of that required for the hexammine. At present the most satisfactory explanation of these phenomena is that ammonia, first taken up as a solid solution, ammonolyzes the salt to the mixture of gray color. This interpretation is confirmed by the fact that the gray color cannot be discharged by decrease of the ammonia pressure, and that liquid ammonia extracts what appears to be ammonium chloride from the solid. The reaction, however, is so slow and incomplete that it could not be satisfactorily studied at the temperatures of our experiments.

It is evident from these results that Ephraim confused the gray color which resulted from the action of an excess of ammonia on the hexammine with the color of the hexammine itself. Furthermore, in experiments on dissociation pressures in this system the formation of the gray material must be avoided because it retards greatly the attainment of equilibrium and obscures the interpretation of analytical data. Unfortunately it is formed more rapidly at high temperatures, at which the dissociation pressures of the ammines would otherwise be more readily determined, and therefore the work must be done at temperatures at which the reactions are very slow.

The System Chromous Chloride–Ammonia.—Because of the difficulties just discussed, dissociation pressures of the various ammines could not be determined in the usual way by observing the pressures which are ultimately reached by mixtures of ammonia and chromous chloride ammines of various compositions. Instead, it was necessary in each case to prepare the mixture of hexammine and pentammine by allowing the former to remain in an evacuated vessel for a short period of time. Ammonia was then admitted and the pressure changes observed. If the pressure fell, its value obviously was above the dissociation pressure of the hexammine; consequently a portion of the gaseous ammonia was removed, and the observations were repeated. If the pressure continued to fall, more ammonia was removed from the gas phase. If the pressure rose, ammonia was readmitted but not in sufficient amount to bring the pressure back to its initial value. By repeated observations made after successive evacuations and readmissions of ammonia, the equilibrium value could be bracketed by approaching it from both sides. Finally an ammonia pressure could be found under which no changes occurred over a period of three or four days. This was taken as the equilibrium value. The procedure was very time-consuming, often requiring several weeks to establish a single point on the pressure composition diagram, but it led to reliable results. The equilibrium pressures thus found at 35.5° are reproduced in Table II and Fig. 1.[4] Compositions represent (moles NH_3)/(moles $CrCl_2$).

TABLE II

Compn.	5.85	5.3	5.19	4.95	4.81	4.54	3.6	3.2	2.95	2.21
Pressure, cm. Hg	23.25	23.25	23.25	3.5	3.5	3.5	3.5	3.5	0.85	0.85
	Hexammine			Pentammine					Triammine	

When the composition of the diammine is reached the pressure becomes immeasurably small, and further removal of ammonia cannot be effected even by raising the temperature to 140–150° for twenty-four hours; at still higher temperatures ammonium chloride is given off. Inspection of the table and figure makes clear that chromous chloride forms ammines

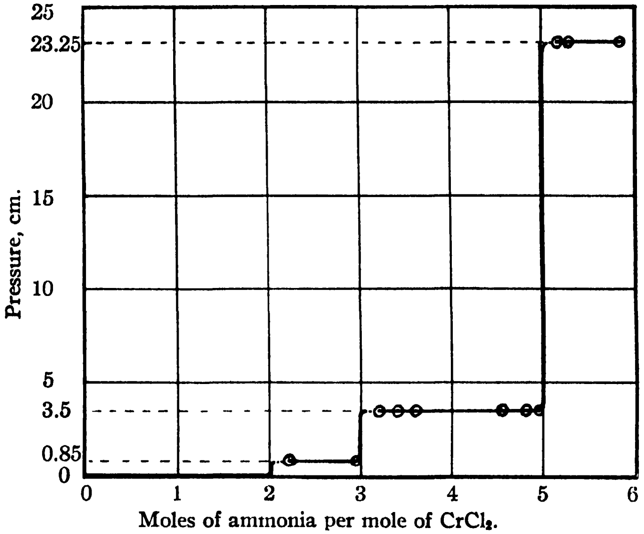

Fig. 1.—System chromous chloride–ammonia at 35.5°.

with 6, 5, 3 and 2 molecules of ammonia, respectively. The equilibrium pressures for the pentammine were also determined at 41 and 50° and found to be 5.7 and 10.3 cm., respectively; for the triammine the value is 5.38 cm. at 62°. These values are obtained from measurements at a single composition in each case. Since only two measurements were made for the triammine at 35.5°, because of the slowness with which equilibrium is reached at this temperature, measurements at the compositions 2.95, 2.54, 2.3 and 2.21 were made at 42°, and gave the constant value 1.1 cm. This confirms the conclusion drawn on the basis of the small number of determinations at the lower temperature.

Preparation of the Lower Ammines.—The dissociation pressures show

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(4) In interpreting the curve it should be borne in mind that the abrupt changes shown in the pressure are changes in the equilibrium values. At no composition is there a rapid transition from one constant pressure to another.

that the data of both Peters and Ephraim are erroneous in several respects, for they recognized only a hexammine and a triammine. In many instances their data do not correspond to equilibrium conditions.[5] Ephraim's failure to obtain a constant vapor tension as ammonia is removed from the hexammine has been shown to be due to an extremely slow attainment of equilibrium. He also assigns to the triammine the vapor tension which, according to our results, is more nearly that of the pentammine. Our observations also indicate confusion in the earlier descriptions of the properties of the ammines, particularly with regard to their colors. It was, therefore, desirable to prepare each of them in as pure condition as possible.

If a vessel containing a sample of the hexammine is continuously evacuated at room temperature, the pressure falls steadily to about four millimeters, during which time there is a gradual change in color from blue to deep violet. The hexammine is thus completely decomposed; small amounts of ammines other than the pentammine are removed by allowing the material to stand for some time in contact with ammonia at a pressure just below the dissociation pressure of the hexammine.

Removal of ammonia from the pentammine is much hastened by raising the temperature to 60 or 70°. If the sample is not heated too long, the gray material described above is not formed in appreciable quantity, probably because of the low pressure at which removal is effected. At a composition of approximately three moles of ammonia to one of chromous chloride, the color has changed again, this time to a light blue, and the equilibrium pressure has changed to that of the triammine. In similar fashion the sage green diammine can be prepared. The data concerning these ammines are summarized in Table III.

TABLE III

Ammine	Analysis,[a] moles NH_3 per mole $CrCl_2$	Dissociation pressure, cm.[b]	Color
$CrCl_2.6NH_3$	6.01	23.25	Dark blue
$CrCl_2.5NH_3$	4.95	3.5	Violet
$CrCl_2.3NH_3$	3.03	0.85	Light blue
$CrCl_2.2NH_3$	2.00	Practically zero	Sage-green

[a] Calculated from the average of data obtained from the purest sample.

[b] Values for the dissociation pressures at other temperatures are given on p. 3974.

The Reactions of Chromous Chloride Ammines with Chlorine.—It seemed possible that reaction of chlorine with the diammine, which because of its low ammonia tension is particularly suited to such a study, might lead to the formation of a diammine of chromic chloride. This

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(5) Ephraim gives the vapor tension of the hexammine as

Temperature, °C.	0	13	16	27	33.5	43.5
Pressure, mm.	104	194	228	387	517	744

For the violet intermediate product which he calls the triammine, he gives the following tensions

Temperature, °C.	44	59.5	72	86	92	95
Pressure, mm.	45	97	198	433	618	730

substance would have peculiar interest because the normal coördination number of trivalent chromium is six. For carrying out the reaction, the reaction tube was connected into a closed system provided with a manometer in which the mercury was protected from the chlorine by a small layer of concentrated sulfuric acid. The system was evacuated and pure dry chlorine admitted. There was no apparent reaction in the cold, but at 250° the absorption of chlorine became noticeable and resulted in the formation of a reddish-violet hygroscopic substance which was unstable in air. At approximately 275° the color changed to a deep purple and ammonium chloride was evolved. At still higher temperatures complete reaction to form chromous chloride, ammonium chloride and nitrogen occurred. All the intermediate stages seemed to be mixtures of variable composition.

The fact that chlorine should oxidize the ammonia in the complex molecule without affecting the powerfully reducing chromous ion was unexpected. A similar reaction occurs with the triammine; this may be due to the fact that by oxidation of ammonia the diammine is first formed and then reacts further with chlorine. The essential reaction of chlorine with the ammines is oxidation of the ammonia; the color changes were shown by direct test to be due to interaction of hydrogen chloride formed by this oxidation, on the residual amines. The product of the reaction of hydrogen chloride on the ammines is a mixture which could not be separated into its components.[6]

The authors take pleasure in acknowledging their indebtedness to Professor W. C. Johnson, who supervised the work for a time while the senior author was out of residence, and to Dr. Anton B. Burg for his aid in many technical problems.

Summary

A blue hexammine, a violet pentammine, a light blue triammine, and a sage-green diammine of chromous chloride were prepared.

Methods were developed for determining the dissociation pressures of these substances in spite of the fact that equilibrium is attained very slowly. Dissociation pressures of $CrCl_2{\cdot}6NH_3$, for $CrCl_2{\cdot}5NH_3$, and for $CrCl_2{\cdot}3NH_3$ were determined at 35.5°; in addition ammonia tensions for the pentammine were measured at 41 and 50°, and for the triammine at 42 and 62°.

Chlorine oxidizes the ammonia of these complex chromous compounds but does not affect the chromous nucleus.

CHICAGO, ILLINOIS

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[6] Analysis of the first sample of this material showed the following ratio: chromium 1, ammonia 1.488, chlorine 3.55. This would indicate the formation of a compound of the type $2CrCl_2{\cdot}3NH_4Cl$. Later samples failed to duplicate first results.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Kinetics of the Reduction, in Acid Solution, of Hydrogen Peroxide by Iodide Ion

BY HERMAN A. LIEBHAFSKY AND ALI MOHAMMAD

Introduction

The first successful quantitative investigation in chemical kinetics, completed in 1866 by Harcourt and Esson,[1] proved that the rate of the reaction

$$H_2O_2 + 2H^+ + 3I^- = 2H_2O + I_3^- \qquad (1)$$

is proportional to the amounts of peroxide and iodide present, and that it is "accelerated" by the addition of acid. A quarter century later Magnanini,[2] in a remarkable investigation, which we shall subsequently consider in some detail, demonstrated how this "acceleration" is related to the acid added. Noyes,[3] interested chiefly in clarifying the fundamental concept "order of a chemical reaction," was the first to point out that Magnanini's results and those of Scott[3a] followed a differential equation of the form

$$d(I_3^-)/dt = k_1^\circ(H_2O_2)(I^-) + k_1(H_2O_2)(I^-)(H^+) \qquad (2)^4$$

He regarded the "accelerating" action of hydrogen ion as catalytic even though this substance is consumed in the reaction. Other investigators,[5] however, have preferred to interpret Equation 2 in terms of two independent rate-determining steps, which may be formulated

$$H_2O_2 + I^- \xrightarrow{k_1^\circ} H_2O + IO^- \qquad (3)$$

$$H_2O_2 + H^+ + I^- \xrightarrow{k_1} H_2O + HIO \qquad (4)$$

Reaction 3 is a compensating reaction in the catalytic decomposition of hydrogen peroxide by the iodine–iodide couple, which has been much investigated;[6] Reaction 4, however, seems to have been studied recently only as a means of determining hydrogen peroxide.[7] Consequently, the specific rate of the former reaction (k_1° = 0.69 at 25°) is well established, while no very accurate value can be assigned to that of the latter.[8]

Reactions whose rate laws involve hydrogen ion in the manner of Equation 2 are not very common; one of this type is the reduction of iodate by hydrogen peroxide,[9] the study of which suggested a reinvestigation of Reaction 1 in order that accurate values for the heats of activation of Reactions 3 and 4 might be secured for comparison with those of the corresponding rate-determining steps involving iodate ion. Such a reinvestigation may be regarded, also, as contributing to research of a more general type that has long been under way in this Laboratory,[6a,b,9,10] namely, the interaction of hydrogen peroxide and iodine compounds of all valences. Further, Reactions 3 and 4 are simple, and their rates can be measured accurately; consequently, they are well adapted to studies of the kinetic salt effect. And, finally, they possess low apparent heats of activation so that they may be investigated over a considerable range of temperatures for the purpose of determining how these heats vary with the temperature.

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(1) (a) Harcourt and Esson, *Phil. Trans. Roy. Soc.*, **157**, 117 (1867) (second paper) and (b) Harcourt, *J. Chem. Soc.*, **20**, 460 (1867).

(2) Magnanini, *Gazz. chim. ital.*, **21**, 476 (1891).

(3) (a) Noyes, *Z. physik. Chem.*, **18**, 119 (1895); (b) **19**, 601 (1896).

(4) As in previous communications, ( ) will be used to denote concentrations in moles per liter, and $\longrightarrow$ will be restricted to reactions which may be rate-determining.

(5) Bray, *Z. physik. Chem.*, **54**, 463–97 (1906).

(6) (a) Abel, *ibid.*, **136**, 161 (1928); **96**, 1 (1920). In the latter reference, a comprehensive historical summary of earlier work by Abel and others is given. (b) Liebhafsky, THIS JOURNAL, **54**, 1792 (1932); (c) *ibid.*, **54**, 3499 (1932).

(7) Bray and Livingston, *ibid.*, **50**, 1654–65 (1928).

(8) For these constants at 25°, Bray in 1906 chose the values k_1° = 0.60 and k_1 = 16; since the first value is too low, the second is probably too high.

The Experimental Method

Results Obtained at 25°.—An examination of Equation 1 will reveal that tri-iodide ion is formed as the reaction proceeds; the simplest experimental conditions obtain when no appreciable change in the concentration of iodide ion results from such complex ion formation. One way of realizing these conditions is by using an amount of hydrogen peroxide so small that no great change in (I^-) has resulted when reaction is complete; if (H^+) and (I^-) are comparable, then (H^+) also will be (nearly) constant during the experiment. Under these conditions the rate law, Equation 2, will assume the simple form

$$d(I_3^-)/dt = -d(H_2O_2)/dt = k'(H_2O_2) = [k_1^\circ(I^-) + k_1(H^+)(I^-)](H_2O_2) \qquad (5)$$

So long as the experimental method employed shows k' to be unchanged during the course of an experiment, average values of (H^+) and (I^-) may be used to calculate k_1° and k_1. All experiments that were carried out by the method described below (the "analytical method") meet this test.

In such experiments all the reaction mixture (c. p. sodium iodide and perchloric acid were used) except the peroxide, contained in a glass-stoppered flask, was placed in a thermostat at the desired temperature and shielded from direct light. After temperature equilibrium had been reached, a measured volume of hydrogen peroxide solution from a reservoir in the bath was added to start the reaction, zero time being taken when the addition was half complete. From time to time 25-cc. samples were withdrawn with a pipet and permitted to flow into 125 cc. of water at 0°, in order to retard Reaction 1 by cooling and dilution. The time of sampling was recorded as the time when the pipet was half emptied. So soon as was convenient,[11] these samples were titrated with a 0.004 N thiosulfate solution. The increase in the thiosulfate titer of the samples served to measure the rate of Reaction 1.

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[9] Liebhafsky, THIS JOURNAL, 53, 896 (1931). No completed investigations are available, but the preliminary results obtained in this Laboratory by Liebhafsky indicate definitely that the rate laws for the reduction of hydrogen peroxide by bromide and by chloride ions have the form of Equation 2; the approximate values at 25° of the specific rates for the steps analogous to Reaction 3 are 2×10^{-7} (chloride) and 2.3×10^{-4} (bromide).

[10] (a) Bray and Liebhafsky, THIS JOURNAL, 53, 38 (1931); (b) Bray and Caulkins, *ibid.*, 53, 44 (1931); (c) Liebhafsky, *ibid.*, 53, 2074 (1931); (d) Bray, *Chem. Rev.*, 10, 172 (1932).

The evaluation of k', which is independent of concentration units, is easily accomplished. If a represents the thiosulfate titer of a sample when reaction is complete, and x represents this quantity at time t, then

$$d(x)/dt = k'(a - x) \tag{5a}$$

for a is proportional to the initial (H_2O_2), and $(a - x)$ to (H_2O_2) at time t. Values of $\log (a - x)$ for experiments done by this method were plotted as ordinates against the time (*cf.* Fig. 1 and Table I); the slopes of the resulting straight lines, when multiplied by 2.303, gave the values of k' for these experiments.

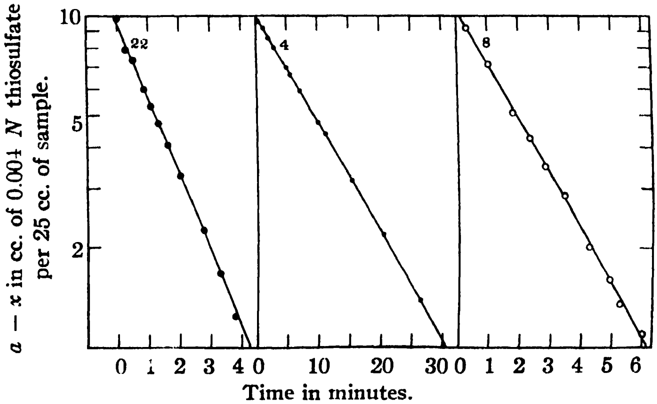

Fig. 1.—Detailed experimental results at 25°. The plot is on *semi-logarithmic* paper. The composition of each reaction mixture is given in Table I (*cf.* footnote b).

To obtain k_1^0 and k_1, values of k' obtained from experiments at various concentrations of iodide and of hydrogen ion are necessary. If Equation 5 is valid, experiments at constant (H^+), but at different (I^-), should yield

(11) A sample was usually titrated within one minute after its withdrawal; in exceptional cases, when successive samples were taken rapidly, titration was postponed longer—but never for more than ten minutes. During the interval between the time of a sample and the time of its titration, the samples were kept in the dark at 0°.

The amount of iodine formed in a sample while it awaited titration was obtained as follows. Before the beginning of a run a blank, having the volume and composition that would result from diluting a sample of the reaction mixture before iodine formation had begun, was prepared and kept in the dark at 0°. When the experiment was over this blank was titrated with thiosulfate. If C represents the amount of iodine formed during this time (t minutes), then C/t represents the rate of its formation (C is so small that (H^+) and (I^-) and (H_2O_2) in the sample may be regarded constant). If Δt minutes have elapsed between the time of dilution and the time of titration in a sample of reaction mixture, the iodine formed in this interval is equivalent to $(\Delta t/t) \times ((a - x)/a) \times C = d$; the second factor corrects for the difference in the peroxide concentrations of the blank and of the actual sample (*cf.* Equation 5a above). This amount of iodine, d, which must be subtracted from the iodine equivalent to the thiosulfate titer of a sample, was always small; it seldom exceeded 0.5% of the latter, and was usually very much less.

k' values that lie on a straight line intersecting the origin when these are plotted as ordinates against (I^-); from the slope of this line, which is equal to $k_1^\circ + k_1(H^+)$, the specific rates are easily calculated. Curve I, Fig. 2, gives the results of a series of such experiments; its slope has the value 1.128. If, on the other hand, (I^-) is kept constant for a series of experiments, and (H^+) is varied, Equation 5 demands that the resulting k' (or $k'/(I^-)$) values yield a straight line intersecting the ordinate axis when they are plotted against (H^+) as abscissa. If $k'/(I^-)$ values are thus plotted, the intercept on the ordinate axis should give directly the value of k_1°; the slope, that of k_1. Curve II, Fig. 2, represents the results of two such series of measurements: its intercept yields k_1° = 0.69, in perfect agreement with the recent measurements of

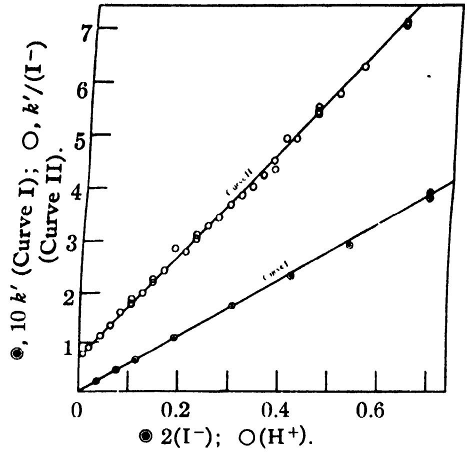

Fig. 2.—Summary of rate measurements at 25° in perchloric acid–sodium iodide solutions.

TABLE I

EXPERIMENTAL RESULTS AT 25°. INITIALLY (H_2O_2) IS APPROXIMATELY $8(10^{-4})$ MOLES/LITER. AVERAGE VALUES FOR (H^+) AND (I^-) ARE GIVEN

Data for Curve I, Fig. 2 (H^+) = 0.0413; (I^-) variable		Data for Curve II, Fig. 2 (I^-) = 0.0572; (H^+) variable				Data for Curve II, Fig. 2 (I^-) = 0.0614; (H^+) variable	
$(I^-) \times 10^2$	$k' \times 10^2$	$(H^+) \times 10^2$	$k'/(I^-)$	$(H^+) \times 10^2$	$k'/(I^-)$	$(H^+) \times 10^2$	$k'/(I^-)$
1.86	2.1	0.762	0.770	37.7	4.51	10.4	1.81
3.78	4.2	2.03	.893	42.0	4.92	10.4	1.76
5.71	6.4	4.20	1.120	46.2	5.38	10.4	1.78
9.58	10.8	6.23[b]	1.320	46.2	5.44	14.6	2.18
15.40	17.3	8.34	1.608	46.2	5.52	14.6	2.25
21.20	23.0	12.55	1.98	50.4	5.78	18.8	2.84
27.00	29.0	16.76	2.41	55.0	6.28	23.0	3.03
34.71[b]	38.0	20.97	2.78	63.1	7.10	23.0	3.10
34.71	39.2	25.18	3.27	63.1	7.05	27.3	3.43
k_1° = 0.69;		29.38	3.68	84.1[b]	9.20[c]	31.5	3.86
	k_1 = 10.6	33.60	4.01	k_1° = 0.69;		35.7	4.23
		37.8	4.33		k_1 = 10.4	39.9	4.92
						k_1° = 0.69;	k_1 = 10.4

[a] Initial (final) values of (H^+) and (I^-) may be obtained by adding (subtracting) $8(10^{-4})$ moles/liter to (from) the average concentrations.

[b] In Fig. 1, (I^-) = 0.3471 is No. 8; (H^+) = 0.0623 and 0.841 are Nos. 4 and 22, respectively.

[c] This value of $k'/(I^-)$ coincides exactly with Curve II, but it could not be plotted in Fig. 2 because of the restricted scale.

Liebhafsky;[6b] its slope, 10.4, gives the value of k_1; both values are for 25°. Using $k_1^0 = 0.69$ and $(H^+) = 0.0413$, the acid concentration corresponding to the k' values for Curve I, $k_1 = 10.6$, is obtained from the slope of this curve. The agreement of these independently obtained values of k_1 is satisfactory. We may thus consider Equation 5 to be established definitely over a concentration range sufficiently large.

Reëxamination of Magnanini's Data.—The desirability of comparing Magnanini's results with ours led us to reëxamine his data.[12] It was then observed that Magnanini's rate constants decreased during each run, and that this decrease became pronounced earlier in experiments in which the absolute rates were higher; *e. g.*, in experiments at high (H^+). In Table II are given the data for the experiments with the lowest (in which only hydriodic acid was used to furnish H^+) and the highest (H^+) in his series of measurements with hydrochloric acid. Values of $\Sigma(I_2)$, the sum of (I_2) and (I_3^-), are those given by Magnanini; and the concentrations of I_3^- were computed with the aid of the equilibrium constant $(I^-)(I_2)/(I_3^-) = 0.00140$ at 25°.[13] The "corrected" values of $k'/(I^-)$ resulted from Magnanini's when the latter were multiplied by $[(I^-) + {}^1/_2(I_3^-)]/(I^-)$.[14] Although this correction is only approximate, the constancy of the "corrected" values is sufficiently good to leave no doubt that failure to consider the diminution in (I^-) resulting from I_3^- formation caused Magnanini's rate constants to decrease as the reaction proceeded.

In Fig. 3 Magnanini's results with the strong acids are plotted, the values of $k'/(I^-)$ used corresponding to measurements over the first time interval at each concentration of acid; correction for I_3^- formation has been made.[14] The slope of the line is 11.0, a value of k_1 in excellent agreement with ours. Had no correction for I_3^- been made, and Magnanini's results plotted as he gives them, this agreement would not have been altered, since this correction is very small during the initial time intervals; a plot of his

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[12] The results of Scott[3a] cannot yield an accurate measure of k_1, since (H^+) in his experiments varied only from 0.005 to 0.020; under these conditions Reaction 4 contributes less than 25% to the absolute rate.

[13] Jones and Kaplan, THIS JOURNAL, **50**, 1485 (1928).

[14] Magnanini obtained C($100\ C = k'/(I^-)$; the factor 100 is necessary because of a difference in concentration units) from the integrated form

$$C = \frac{1}{t}\,\frac{1}{2a - 2x} - \frac{1}{2a}$$

of the second order rate law for the special case $2a = b$ (we have used only those of his experiments in which this restriction holds). Here a and x have the meanings of Equation 5a and b represents the initial (HI), also the initial (I^-). x further represents $\Sigma(I_2)$ at time t; $\Sigma(I_2) = (I_2) + (I_3^-)$. Now, this evaluation of C implicitly assumes that $(I^-) = (b - 2x)$ as the reaction proceeds; and, since $(b - 2x)$ really represents $(I^-) + (I_3^-)$, values of C will be too small when (I_3^-) is appreciable. At time t the rate calculated by use of C (or of $k'/(I^-)$) must be multiplied by $[(I^-) + (I_3^-)]/(I^-)$ if the actual rate is to be obtained; at $t = 0$, however, (I_3^-) is negligible and this multiplicative factor is $(I^-)/(I^-)$, or unity. The mean of these two factors, or $[(I^-) + {}^1/_2(I_3^-)]/(I^-)$ may thus be used as an average correction for C, if this rate constant has been calculated for the interval $t = 0$ to $t = t$; multiplication of C by this average factor will give approximately the value that would have been obtained had the correction for I_3^- formation been included in the differential equation for the rate; the evaluation of C from this exact expression for the rate would naturally be very laborious.

TABLE II

DETAILED RESULTS OF TWO EXPERIMENTS BY MAGNANINI

(a) "No acid added" (Ref. 2, p. 479)

Initially, $(H^+) = (I^-) = 2(H_2O_2) = 0.0111$; temperature, 25°

Time in minutes	5	15	30	60	120
$\Sigma(I_2) \times 10^4$	2.40	6.40	11.10	17.85	25.35
$(I_3^-) \times 10^4$	2.00	5.00	8.2	11.8	13.5
Magnanini $k'/(I^-)$	0.82	0.78	0.75	0.71	0.63
Corrected $k'/(I^-)$	.83	.80	.79	.77	.71[a]

[a] The remaining decrease in the "corrected" values is due principally to the decrease in (H^+) resulting from the progress of Reaction 1; this causes a decrease in the rate of Reaction 4, for which Magnanini made no allowance in his calculations. The corrected values for the "50 HCl" experiment are much more nearly constant.

(b) "50 HCl" (Ref. 2, p. 482)

Initially, $(I^-) = 2(H_2O_2) = 0.0111$; $(H^+) = 0.567$; temperature, 25°

Time in minutes	3	5	8	10	12	14
$\Sigma(I_2) \times 10^4$	1.01	1.47	1.97	2.25	2.47	2.64
$(I_3^-) \times 10^4$	7.5	10.0	12.0	13.0	13.6	13.8
Magnanini $k'/(I^-)$	6.66	6.44	6.19	6.12	5.98	5.84
Corrected $k'/(I^-)$	7.03	6.90	6.76	6.80	6.75	6.70

uncorrected constants yielded $k_1 = 10.6$, in perfect agreement with the results from Fig. 2.

With hydrochloric and nitric acids Magnanini obtained identical results over the entire concentration range he studied; but with sulfuric acid he found that the effectiveness of the acid in "accelerating" Reaction 1 decreased with the stoichiometric concentration thereof, as the solid circles in Fig. 3 show. This decrease is due principally to an increase in the concentration of the weak acid, HSO_4^-, at the higher concentrations of sulfuric acid; for this reason the ratio $(H^+)/\Sigma(H^+)$ becomes smaller as (H_2SO_4) increases. If kinetic salt effects are absent, rate measurements may, under proper conditions, yield the dissociation constant of HSO_4^-, a circumstance which has already been turned to use in this Laboratory.

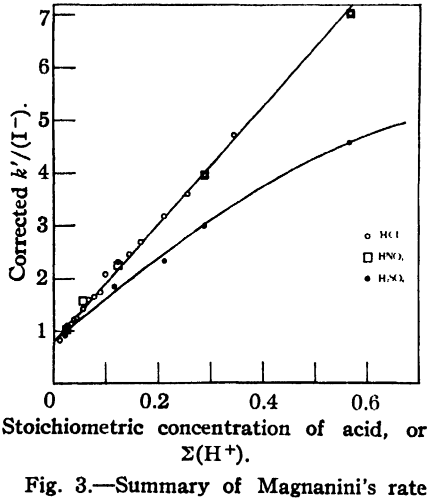

Fig. 3.—Summary of Magnanini's rate measurements in hydriodic acid solutions with hydrochloric, nitric or sulfuric acid added.

Magnanini also employed weaker acids, such as acetic and oxalic, for additional rate measurements. The results of these we have not recalculated because of the great difference in (H^+) and $\Sigma(H^+)$, which renders these acids almost ineffective in "accelerating" Reaction 1. It is worthy of special mention that Magnanini, over forty years ago, appreciated the cause of this ineffectiveness.

We cannot dismiss Figs. 2 and 3 from consideration without calling attention to the absence of appreciable kinetic salt effect for Reaction 4; did such an effect exist in the ionic strength range investigated, the excellent agreement of the various k_1 values could not have been secured.

Effect on the Reaction System of Changing the Temperature.—The results of experiments showing how the specific rates vary with temperature are given in Table III and plotted in Fig. 4. Most of these data were obtained from Curve II, Fig. 2, and from similar curves at 0, 15 and 40°; the rest (the solid circles) are hitherto unpublished values of k_1°, which Liebhafsky determined by following the rate of oxygen evolution from (initially neutral) solutions containing iodide ion and hydrogen peroxide (*cf.* Ref. 6b). From these combined data we deduce

$$k_1^\circ = 4.91(10^9)e^{-13,400/RT} \quad (6a)$$

$$k_1 = 4.58(10^8)e^{-10,450/RT} \quad (6b)$$

Over the temperature ranges investigated, Equations 6 will give to within 3% ($\epsilon = 0.0130$ for $\log k_1^\circ$ and 0.0122 for $\log k_1$)[15] the values of k_1° and k_1; for the average

TABLE III

VALUES OF SPECIFIC RATES AT DIFFERENT TEMPERATURES

Results of measurements in acid solution, by the "analytical" method. $(I^-) = 0.0572$ moles/l.; (H^+) variable

T, °C.	0.0	15.0	25.0	40.0
k_1°	0.094	0.35	0.69	2.19
k_1	2.05	5.50	10.4	22.9

Results of measurements[a] in slightly alkaline solution, by the oxygen evolution method

T, °C.	15.4	20.8	25.1	30.0	31.1	35.7	41.3	45.0	49.4
k_1°	0.344	0.528	0.71	0.98	1.19	1.55	2.50	3.14	4.23

[a] These measurements were made at different iodide concentrations, all below 0.1 M.

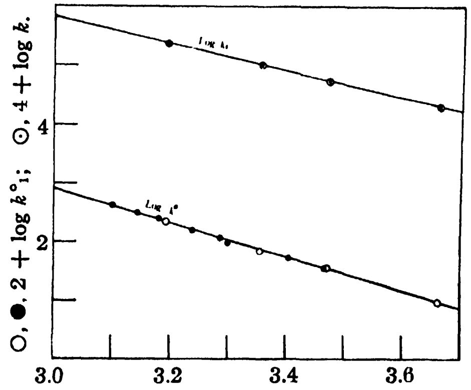

Fig. 4.—Variation of the specific rates with temperature.

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[15] No systematic procedure is uniformly followed in determining the values and the accuracies of the parameters A and Q defined by $k = Ae^{-Q/RT}$. We have employed the following approximate method, which, though not mathematically rigorous, is simple and yields reasonable values for our errors in Q. Values for log k are plotted as ordinates against $1/T$, sufficiently large scales being employed. By successive trials, that line is found for which $\epsilon = \sqrt{\Sigma d^2/(n-2)}$ is a minimum. ϵ is the average error in log k, d is the vertical distance of any point from the line (or curve), n is the number of different temperatures for which observations exist. (In calculating ϵ, n must be diminished by 2 be-

errors in the apparent heats of activation, we have computed $\epsilon_{Q_1^\circ} = 105$ and $\epsilon_{Q_1} = 120$ calories. Obviously, these data extend over a larger temperature range and possess higher accuracy than is usual.

The relationship of the data in Equation 6a to those in 6b is roughly that which obtains also for the similar rate-determining steps involving iodate ion and hydrogen peroxide;[9] a complete discussion of this significant relationship is best postponed until the complete data are available for the analogous pairs of rate-determining steps by which chloride and bromide ions reduce hydrogen peroxide.

One point, however, may be considered briefly. It is well known that, for diverse reasons, the apparent *heat* of activation, Q, defined by

$$\mathrm{d} \ln k/\mathrm{d}\, 1/T = -Q/R \tag{7}$$

should normally vary with the temperature. Using the results of investigations in the kinetics of gaseous reactions to guide us,[16] we may write

$$-\frac{Q}{R} = -\frac{E}{R} - \frac{T}{2} + (n - 1)T - sT - \frac{1}{R}\sum_{i=1}^{i=m} \Delta H_i \tag{8}$$

In this equation E represents the true *energy* of activation, *i. e.*, the minimum energy that a molecular system can have if the reaction in question is to occur; $-T/2$ is to be included only if the reaction is bimolecular, and because the collision number varies as $T^{1/2}$; $(n - 1)T$ represents the effect on Q of the change in energy distribution that accompanies a change in temperature if $2n$ "squared terms" contribute to the activation energy; $-sT$ results if the probability of reaction for a molecular species increases in somewhat the way assumed by Kassel[17] with the amount of energy in

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cause 2 values of log k are necessary to fix A and Q. Unless there are special reasons for not doing so, it seems advisable to plot for each temperature only the arithmetic mean of the observations thereat. If d is noticeably larger or smaller at high temperatures than at low, a system of weighting may be introduced.)

We have taken $\epsilon_Q = 2.3R\epsilon/\Delta(1/T)$ calories, $\Delta(1/T)$ corresponding to the temperature interval over which measurements exist. This method of calculating the error in Q emphasizes the importance of measuring log k over a large temperature range; the method probably gives values of ϵ_Q that become increasingly too large as $\Delta(1/T)$ becomes smaller, n remaining constant.

If Q deviates appreciably from constancy in the temperature range investigated, this method of calculation must be modified; we suggest that it be used to calculate values of Q and ϵ_Q for sections of the temperature range over which the former may be considered constant.

Since ϵ_A is of less importance than ϵ_Q, it need not usually be given; one must always remember, however, that an uncertainty in Q implies a corresponding uncertainty in A.

In work of high precision, the change in the concentrations of reactants due to thermal expansion of the reaction mixture should be considered; the effect of such expansion will be to render the values of rate constants measured at T°, and calculated by using the concentrations of solutions at room temperature, approximately $(m - 1)\,\Delta$ per cent. too low (here Δ is the percentage change in the volume of water between T° and room temperature, and m is the order of the reaction). In none of our work is this correction appreciably over 1%, and we have not applied it; Equations 6, therefore, are based on concentrations of solutions at room temperature, which is convenient.

(16) For an excellent discussion of the heat of activation in gaseous reactions, the reader is referred to Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., New York, 1932.

(17) Kassel, *Proc. Nat. Acad. Sci.*, **16**, 358 (1930). As one second order reaction for which Q increases with T as though the probability of reaction varied with the energy of the reacting molecular species approximately in the manner he postulates, Kassel cites the classical decomposition of gaseous hydrogen iodide, so thoroughly and carefully investigated by Bodenstein [*Z. physik. Chem.*, **29**, 295 (1899)]. Bodenstein gave two empirical equations to reproduce Q as a function of T; Kassel modified

excess of E that this system possesses (for systems with energy less than E the reaction probability is zero); and the last term is obtained by summing the heats of reaction for all equilibria involving a substance concerned in the rate-determining step.[18] (If such an equilibrium is not always maintained, its contribution to Q may not always be the ΔH of the corresponding reaction; in this event, its contribution to $\partial Q/\partial T$ will not be merely ΔC_p, the change in heat capacity, but must compensate also any significant change in the nearness to which the equilibrium is appproached at the different temperatures.)

For the temperature coefficient of Q we now have

$$\partial Q/\partial T = R\left(0 + {}^1/_2 - n + 1 + s - \sum_{i=1}^{i=m} \Delta C_{p_i}\right) \tag{9}$$

if E, n, and s are constant.[19] Equation 9 is to be regarded as tentative, even in form, until accurate experimental material has accumulated in an amount sufficient to render sound judgment possible.

If the errors in Q_1° and Q_1 are not larger than we have calculated, $\partial Q/\partial T$ is not greater than, say, 6 cal./deg. for either Reaction 3 or 4. In the interpretation of these results, the possibility that $\partial Q/\partial T$ is very small because some of the terms in Equation 9 are opposed in sign must not be disregarded; to render this possibility less likely, additional measurements are to be made on analogous reactions. We shall conclude this discussion by pointing out that aqueous solutions may prove better adapted to testing Equation 9 than are gases; for what disadvantage the former suffer in offering a more limited temperature range (0 to 100°, under ordinary conditions) may be more than compensated by the opportunities for more accurate rate measurements which they usually give. The interpretation of these measurements, however, will normally be less certain for the solutions because of the enhanced importance of all kinds of intermediates, which is reflected in the last term of Equation 9; that is, the order of a

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the simpler of these by decreasing the coefficient of the log T term from 16 to 13, a change not greater than the uncertainty in the value of this term; the corresponding value of s is $13 + 2 - {}^1/_2 = 14{}^1/_2$.

Bodenstein's data are discussed by Hinshelwood [*cf.* Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford, 1929, Fig. 1a, p. 42, and pp. 47 and 48)]; but the significant variation of Q with T, given by Bodenstein, has not been mentioned. Calculation of the Q values for the successive pairs of temperatures (*cf.* p. 48) will show that, in spite of irregularities presumably due to slight experimental inaccuracies, Q does decrease with decreasing T.

(18) For convenience we may group the hydration equilibria, the formation and decomposition of Debye-Hückel "clusters," the closely related repulsion process between ions of like sign, and similar reactions, with the better defined equilibria (such as, for example, the hydrolysis equilibrium of iodine in the oxidation of hydrogen peroxide by that substance, *cf.* Ref. 6c) that may influence a rate-determining step.

(19) There seems to be no reason for assuming E to be in any way a function of T; the temperature concept appears meaningless for a molecular system undergoing chemical transformation since such a system is probably effectively isolated at the instant chemical change occurs. Further, it should be mentioned that, in writing Equations 8 and 9, we have tacitly assumed any steric factor concerned in a successful collision, such as the necessity of proper orientation, to be unaffected by a change in temperature. Also, in these equations, we have assumed, as is usually done, that the chance of an energy greater than E in $2n$ "squared terms" is given by

$$[e^{-E/RT}\,(E/RT)^{n-1}]/(n-1)!$$

an approximation sufficiently good so long as E/RT is large.

reaction in solution, coupled with data like those in Equations 6, indicates far less definitely the *intimate mechanism* of a rate-determining step than does the same information in the case of a gaseous reaction—in solutions probably all third-order reactions, and many of the second order as well, involve equilibria, which need not always be established: a third-order reaction might well be unimolecular under one set of limiting conditions, bimolecular under another, and neither alone in the intermediate region. Obviously these complexities render impossible any simple general interpretation of the Arrhenius constant, A,[15] in terms of the collision number Z.

It will be observed that the point of view indicated above differs radically from that just advanced by La Mer.[20]

Summary

1. The rate of the reaction

$$H_2O_2 + 2H^+ + 3I^- = 2H_2O + I_3^- \qquad (1)$$

has for the first time been measured under the simplest experimental conditions, with the result that the law, previously established

$$d(I_3^-)/dt = k_1^\circ(I^-)(H_2O_2) + k_1(H^+)(I^-)(H_2O_2) \qquad (2)$$

has been formally corroborated. Accurate values of k_1 can now be given.

2. The simplest kinetic interpretation of this rate law assumes the rate-determining steps

$$H_2O_2 + I^- \xrightarrow{k_1^\circ} H_2O + IO^- \qquad (3)$$

$$H_2O_2 + H^+ + I^- \xrightarrow{k_1} H_2O + HIO \qquad (4)$$

to proceed simultaneously and independently. At 25°, $k_1^\circ = 0.69$ and $k_1 = 10.5$; these measured values probably do not differ by more than 1% from the true values of these specific rates.

3. An examination of the early work of Magnanini[2] shows it to be in excellent agreement with our results. Certain trends in his rate measurements have been explained.

4. Within the ionic strength range investigated (roughly, from $\mu_c = 0.05$ to 0.5) Reaction 4 is without appreciable kinetic salt effect.

5. We have found

$$k_1^\circ = 4.91(10^9)e^{-13,400/RT} \text{ from 0 to 50°; and} \qquad (6a)$$

$$k_1 = 4.58(10^8)e^{-10,450/RT} \text{ from 0 to 40°} \qquad (6b)$$

Over the temperature ranges investigated, these equations give to within 3% the values of the specific rates. By use of an approximate method, the details of which are described, we have calculated the average error in Q_1° to be 105, and that in Q_1, 120 calories.

6. A brief discussion of the variation with temperature to be expected for the apparent heats of activation of reactions in aqueous solution has been given.

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[20] La Mer (a) THIS JOURNAL, 55, 1739 (1933); (b) *J. Chem. Phys.*, 1, 289 (1933).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF OREGON]

Acetamide as a Solvent

BY O. F. STAFFORD

Assuming a measure of validity for the doctrine that a substance dissolves other substances of its own kind, a most interesting case should be presented by acetamide as a solvent. This substance melts at about 80° to form a fairly mobile liquid. The fact that it contains a methyl group should give it solvent powers for hydrocarbons; its carbonyl group relates it to ketones, esters and acids; its tautomeric hydroxyl group gives it kinship to water and the alcohols; its amino group brings it into line with ammonia and its derivatives, while the ease with which it yields nitrile suggests a relationship to cyanogen compounds. In the field of inorganic chemistry the above considerations are supplemented by the fact that acetamide outranks all but a half dozen substances in the magnitude of its dielectric constant (59.2).

To test these assumptions the approximate solubilities of some 400 organic compounds and about half that number of inorganic compounds have been ascertained. The procedure, in general, was merely to add the substance to fused acetamide (at about 100°) and to note whether much or little would dissolve. Where in any instance the solubility thus appeared to be slight, the influence of higher temperatures was investigated. Sparingly soluble inorganic compounds were not only tested directly, but in most cases were precipitated by suitable double substitution reactions. It is interesting to note that these precipitation reactions occur with the same readiness as in water or ammonia as solvent.

The general results may be summarized by saying that of the 400 organic substances the only one showing no indications of solubility was cellulose. Asparagine, barbituric acid, oxamide and uric acid are sparingly soluble at low temperatures (*i. e.*, below 100°). It is significant that these same substances are but slightly soluble in water and are rated as insoluble in alcohol and ether. The solubilities of the inorganic compounds are strikingly analogous to those in water. Exceptions are presented by potassium perchlorate, the halides of mercury and lead, and the phosphate and oxide of mercury, all of which are more soluble in acetamide than in water.

More specifically, it was found that among organic compounds sixty-five ammonia-nitrogen derivatives (except uric acid), seventeen carbohydrates (excepting cellulose but including starch), sixty-eight dyestuffs, forty-four alcohols, eleven nitro and nitroso compounds and a number of miscellaneous nitrogen derivatives, all dissolve readily. Of the twenty hydrocarbons tested, anthracene, phenanthrene and triphenylmethane are quite soluble. The others are soluble at higher temperatures, but separate out to form two-phase systems at lower temperatures (80 to 120°). Forty-five acids tested are all soluble, but those with very long hydrocarbon chains are less soluble than the others.

Some twenty oxygen compounds were tested, in this class the ethers appearing to be somewhat less soluble than the others.

Among inorganic compounds bismuth nitrate gives a white insoluble compound similar to that formed by hydrolysis or ammonolysis. Mercurous nitrate undergoes some transformation in contact with the solvent. A similar action appears to take place with mercurous halides. Chromates are slowly reduced in acetamide solutions, although even the solution of chromium trioxide (which in color exactly resembles solutions of chromates) is stable for quite a while. The brown silver carbonate precipitate is presumably in the form of silver oxide, as in the case of precipitation from water.

The close analogy between acetamide and water as solvent is proved not only by the close correspondence which is shown by solubilities of inorganic compounds in these two substances but also by the chemical behaviors of dissolved substances. Mention has already been made of the fact that double substitution reactions occur with the same readiness in acetamide solution as in water solution. In such cases the precipitates in acetamide are even similar in appearance to those formed in water, colored sulfides, for example, appearing precisely as when precipitated from water. A search of the literature reveals that conductivity curves for a considerable number of salts in acetamide solution have been determined and that these curves resemble those obtained in water solutions. Furthermore, it has been shown that electrodeposition occurs readily in acetamide solutions with metals not more active than zinc. Numerous instances are described in which acetamide seems to function analogously to water of crystallization.

It follows, therefore, that the expectations enumerated in the opening paragraph of this article are surprisingly substantiated by experiment. Seemingly acetamide has a wider range of solvent powers than any other substance which has been reported.

Eugene, Oregon

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Potassium in Dilute Potassium Amalgams

BY H. E. BENT AND E. S. GILFILLAN

The primary purpose of this investigation was to determine the activity of potassium in amalgams as a function of concentration and temperature. The need for these data arose during the investigation of potassium triphenylmethyl as an electrolyte, and the study of equilibria involving organic free radicals,[1] and alkali metal amalgams.[2] Seven cells have been constructed. The electrolytes have been a water solution of potassium hydroxide, a solution in diethyl ether of the potassium addition compound of organic free radicals and a solution in ethylamine of potassium iodide.[1] We are greatly indebted to Mr. E. S. Fetcher, Jr., who constructed the first of the ethylamine cells used in this investigation. All seven cells gave very good agreement. However, the last two cells were so much superior that these alone were used in computing the final results. In the final section of this paper the bearing of these results on the nature of amalgams is discussed.

Experimental Method

Much of the experimental detail has been described elsewhere.[1]

The method of filling the cell is indicated in Fig. 1. The cell proper (A) has five fingers, permitting the use of amalgams of five different concentrations. At the bottom of each finger is sealed a platinum wire. This was sealed into ordinary Pyrex glass to give a gas-tight joint by using very fine ribbon. Number 40 wire was rolled into a ribbon about one-half millimeter wide. This was drawn through a small constriction and the glass worked in the flame until the joint was tight. Care must be exercised to avoid pulling, as the slightest tension will sever the wire. A safe method is to push the glass together at all times while making the seal. Contact was made outside the cell by pouring mercury into the leads (C).

A handle (B) served to support the cell after all other tubes had been sealed off.

The amalgams were prepared and stored in the flasks (D). They were analyzed by drawing off samples in exactly the same way in which the amalgams were run into the cell. About 99.5% of the equivalent amount of half normal sulfuric acid was added to the amalgam from a weight buret, the flask heated on a steam-bath and air, free from carbon dioxide, slowly bubbled through the amalgam. When the solution became alkaline it was titrated with one-hundredth normal acid (diluted by weight from

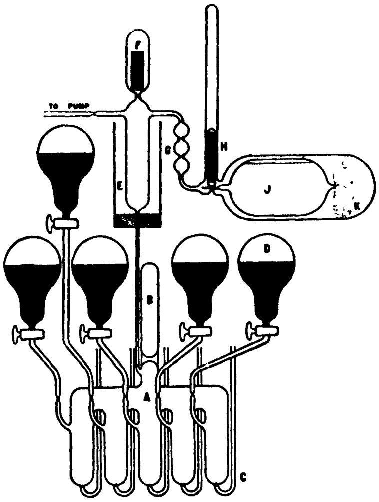

Fig. 1.—Method of filling the cell.

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[1] Bent and Gilfillan, THIS JOURNAL, 55, 247 (1933).

[2] Bent, Dorfman and Bruce, *ibid.*, 52, 1498 (1930); 53, 1786 (1931); 54, 1393 (1932); 54, 3250 (1932).

the half normal acid) using brom thymol blue as the indicator. With the help of a color standard the end-point could be determined within 0.04 mg. of potassium. Addition of the dilute acid was continued until the solution no longer became alkaline after three hours on the steam-bath. The stock half normal acid was standardized by comparison with constant boiling hydrochloric acid prepared according to the directions of Bonner and Titus.[3]

The capsule of ethylamine (J) was padded with glass wool (K) in order to prevent the rebound shattering the tube when the capsule was opened by means of the weight (H). The small bulbs (G) served to throttle the amine and prevent too rapid a rush of vapor into the cell. The amine was condensed in the cell by placing solid carbon dioxide in the tube (E). The potassium iodide was washed from the platinum boat (F) by cooling this tube with a little solid carbon dioxide.

The cell was then placed in a thermostat which consisted of a five-liter Dewar flask filled with water. This was easily controlled manually to 0.01°.

Experimental Results

The data recorded in the following tables were obtained from two cells. The first of these contained amalgams I, VI, VII, VIII and IX and the second contained amalgams II, III, IV, V and VI. The amalgam used by Lewis and Keyes in their cell containing metallic potassium had a composition of 0.2216 weight per cent. potassium, the same as that of amalgam VI. This amalgam was included in both cells in order to make the comparison of the different amalgams with each other and with metallic potassium more simple. These two cells had a resistance of a little more than 100,000 ohms. The composition of the amalgams is given in the first line of Table I.

The e. m. f. data recorded in Table I have already been corrected for three very small errors. The first of these is the calibration error of the potentiometer. These errors amounted to less than 0.016 mv. The second error is a small thermal e. m. f. observed in the potentiometer which was determined by short circuiting the leads. This amounted to 0.02 mv. A third correction was discovered by comparing the potential between amalgams a and c with the sum of the potentials for the pair a and b and for the pair b and c. It was found that the sum was almost invariably less than the single measurement by about 0.04 mv. This can be explained by assuming a contact potential in the switches of this amount. When this quantity was added to the observed readings there was no longer any consistent variation in these differences. The values obtained after making these three corrections are recorded in Table I.

The experimental or observed values are marked Obs. in the table. The difference between these values and those calculated by equation (1) are marked Diff. and will be discussed in the following section. Each recorded value is the mean of a great many readings, several hundred measurements having been made on each cell. Measurements involving an interval of time of but a few minutes did not differ by more than one hundredth of a millivolt. Measurements on different days or after the temperature had been varied usually differed by less than one tenth of a millivolt. The probable error will be discussed later.

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[3] Bonner and Titus, This Journal, **52**, 637 (1930).

Table II gives the data for amalgams containing a solid phase measured against amalgam VI as the reference electrode. These values were always obtained from both lower and higher temperatures and usually did not differ by as much as 0.1 mv. for a given cell. Equilibrium was established by gentle shaking for about an hour at a given temperature.

In order to apply a correction to the e. m. f. data on account of the change in the pressure of the ethylamine with temperature it is necessary to determine the partial molal volume of potassium in these amalgams. Two measurements of the density of the amalgams were made for this purpose. The pycnometer consisted of a 20-cc. Pyrex bulb to which was sealed a capillary of 0.5 mm. inside bore. The final volume was calculated from the position of the meniscus in this capillary as determined by means of a micrometer microscope. The pycnometer was carefully evacuated before filling with the amalgam. The density is given relative to that of mercury at 25°.

Weight fraction of potassium	0.002339	0.004730
Relative density at 25°	0.98275	0.96566

TABLE I

E. M. F. OF AMALGAMS REFERRED TO AMALGAM VI

		No. of amalgam			
		I	II	III	IV
T	Mole fraction[a]	0.026266	0.024438	0.021925	0.019437
50°	Obs.		0.04602	0.03839	0.03050
	Diff.		76	19	−18
35°	Obs.	0.05177	0.04499	0.03746	0.02968
	Diff.	−45	53	5	−23
25°	Obs.	0.05084	0.04418	0.03672	0.02908
	Diff.	−46	48	7	−21
15°	Obs.	0.05002	0.04336	0.03601	0.02850
	Diff.	−58	45	6	−21
0°	Obs.		0.04213		
	Diff.		39		

		No. of amalgam				
		V	VI	VII	VIII	IX
T	Mole fr.	0.015389	0.011267	0.006721	0.001924	0.0001950
50°	Obs.	0.01635				
	Diff.	−18				
35°	Obs.	0.01591		0.02155	0.06323	0.12742
	Diff.	−22		16	4	−38
25°	Obs.	0.01552		0.02099	0.06156	0.12373
	Diff.	−15		22	7	−29
15°	Obs.	0.01522		0.02051	0.05991	0.12003
	Diff.	−18		19	7	−27
0°	Obs.	0.01473		0.01967	0.05736	0.11450
	Diff.	−18		27	15	−22

[a] Each value given for the mole fraction is the average of at least two analyses. The average of the differences between pairs of analyses is 0.000006.

TABLE II

THE E. M. F. OF SATURATED AMALGAMS RELATIVE TO AMALGAM VI

Temp., °C.	Observed e. m. f.		Calcd.	Difference	
0.0	0.00540	0.00527[a]	0.00533	−0.00007	0.00006
5.0	.01330[a]		.01308	− .00022	
7.5	.01719	0.01712[a]	.01708	− .00011	−0.0004
15.0	.02965	0.02959[a]	.02962	− .00003	+0.00003
20.0	.03822		.03842	.00020	
25.0	.04755		.04755	.00000	

[a] These values were obtained from the second cell. All others were obtained from the first cell.

Interpretation of Results

In the discussion of the data the nomenclature of Lewis and Randall[4] and the physical constants of Birge are used.[5]

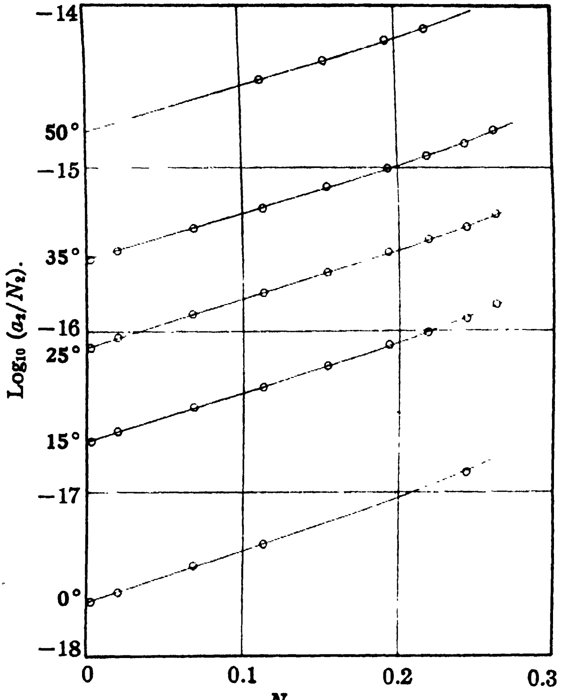

Fig. 2.—The deviation of potassium amalgam from Raoult's law.

The experimental data may be well represented by empirical equations, the use of which, however, is unfortunately time consuming. For convenience, therefore, the data have been represented graphically in Fig. 2

(4) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York.

(5) Birge, *Phys. Rev. Supplement, Reviews of Modern Physics*, 1 (1929). These values are as follows: 0°C. = 273.18 abs.; 1 int. volt equ. = 23,065 calories. R = 1.98643. At. wt. Hg = 200.61. K = 39.096.

and the various computed thermodynamic quantities in Table III. Since four of the quantities given in this table are approximately linear functions of the concentration, rough values may be obtained, at concentrations not given, by interpolation. Only in the case of $\bar{F}_2$ and $\bar{S}_2$ is it not permitted to extrapolate to lower concentrations, as in these cases the partial molal quantity becomes infinite as the concentration becomes zero.

If we take the e. m. f. data of Table I and multiply each value by the faraday equivalent and divide by *RT* we obtain the difference in the natural logarithms of the activity of the potassium in the two amalgams. The values so obtained were found to be represented by the equation

$$\Delta \log_{10} a_2 = \log_{10} N_2 + (2446/T^{0.77700})\, \Delta \left\{ N_2 + \cdot 3430 N_2^4 \right\} \qquad (1)$$

The difference between the experimental value and that calculated from equation (1) is given in the third line for each temperature. If one assumes that the form of the expression is correct, then the probable error can be computed to be 0.04 mv. This is perhaps too small an estimate. If we calculate the error by considering only a series of measurements at a given temperature, we obtain a more conservative estimate of 0.08 mv. We have taken this latter value as a measure of the accuracy of the data.

TABLE III

RELATIVE PARTIAL MOLAL DATA FOR POTASSIUM AMALGAMS

	Temp., °C.	Concn. (mole fraction) 0.001	0.005	0.01	0.02
$\Delta\bar{F}_2$	0	−26,048	−25,018	−24,446	−23,658
	25	−26,019	−24,906	−24,295	−23,465
	50	−25,989	−24,794	−24,145	−23,272
$\Delta\bar{S}_2$	0	−1.16	−4.49	−6.02	−7.73
	25	−1.18	−4.50	−6.02	−7.71
	50	−1.20	−4.51	−6.02	−7.70
$\Delta\bar{H}_2$	0	−26,355	−26,234	−26,081	−25,770
	25	−26,361	−26,237	−26,082	−25,765
	50	−26,367	−26,241	−26,083	−25,760
$\Delta\bar{F}_1$	0	−0.5618	−3.213	−7.432	−19.24
	25	− .6119	−3.471	−7.970	−20.41
	50	− .6618	−3.729	−8.505	−21.56
$\Delta\bar{S}_1$	0	.001999	0.01036	0.02158	0.04687
	25	.001999	.01034	.02147	.04643
	50	.001999	.01031	.02138	.04605
$\Delta\bar{H}_1$	0	− .01520	− .3813	−1.437	− 6.429
	25	− .01550	− .3888	−1.568	− 6.557
	50	− .01580	− .3956	−1.596	− 6.674

In equation (1) the exponent of *T* must be used to five significant figures in computations although the data are not accurate enough to determine this constant beyond the second significant figure.

A more useful way of expressing the data is to refer the activity of the potassium to the pure metal as standard state. This can be accomplished by combining these data with the measurements of Lewis and Keyes.[6] They have found the e. m. f. between metallic potassium and an amalgam in which the weight fraction of potassium is 0.2216 to be 1.0481 and the temperature coefficient to be −0.000272 volt per degree.

Before going farther with these data, however, it is necessary to consider the effect of pressure on the e. m. f. of the cell. During the course of our experiments the pressure of the ethylamine varied by as much as two atmospheres. The effect of this change in pressure may be computed providing we know the partial molal volume of the potassium in the amalgams. This we can compute from the density measurements recorded above. The apparent molal volume, that is, the change in volume when one mole of potassium is added to mercury to give an amalgam of the desired concentration, is found to be 24.57 cc. for the amalgam of weight fraction potassium 0.002339 and 24.61 for the amalgam of weight fraction potassium 0.004730. Since these figures differ so little from each other and the amalgams are very dilute, we may take these values to represent the partial molal volume of the potassium. Taking the volume of one gram atom of potassium as 45.5 cc., we find a change in volume for the cell reaction of 20.9 cc. Since the pressure of ethylamine is about 1.4 atmospheres at 25°, this introduces a correction of only 0.01 mv. in the e. m. f. of the Lewis and Keyes cell, which is much less than their experimental error. The correction in their temperature coefficient is relatively more important, giving a value of −0.000273. These calculations show that the correction becomes important only at the higher temperatures.

We can now combine equation (1) with the measurements of Lewis and Keyes to give the activity of the potassium referred to the solid metal as standard state

$$\log \frac{a_2}{N_2} = -\frac{5{,}695.6}{T} - \frac{27.69}{T^{0.77700}} + 3.3249 + \frac{2446}{T^{0.77700}}\left\{N_2 + 3430N_2^4\right\} \pm 0.0017 \qquad (2)$$

Curves obtained with the aid of this equation are shown in Fig. 2. If Raoult's law were obeyed, $\log a_2/N_2$ would be independent of the concentration and would approach zero at the melting point of potassium.

With the aid of the above equation one may now obtain three relative partial molal quantities, namely, the free energy, entropy and heat content. The reference state for mercury is the pure liquid and for potassium is the solid metal. The relative partial molal free energy is obtained by adding $\log N_2$ and multiplying equation (2) by $RT \log_e 10$, giving

$$\begin{aligned}\bar{F}_2 = {} & -26{,}051 + 4.5739\ \{\log_{10} N_2 + 3.3249\}\ T + \\ & 4.5739\ \{2446(N_2 + 3430N_2^4) - 27.69\}\ T^{0.22300} \pm 2 \qquad (3)\end{aligned}$$

By differentiating equation (3) with respect to the temperature the relative partial molal entropy is obtained

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(6) Lewis and Keyes, This Journal, 34, 119 (1912).

$$\bar{S}_2 = -15.21 - 4.5739 \log_{10} N_2 - 1.0200 \{2446(N_2 + 3430N_2^4) - 27.69\} T^{-0.77700} \pm 0.1 \qquad (4)$$

Finally from the relation $H = F + TS$ the relative partial molal heat content can be obtained

$$\bar{H}_2 = -26{,}051 + 3.5539 \{2446(N_2 + 3430N_2^4) - 27.69\} T^{0.22300} \pm 20 \qquad (5)$$

Four equations may be obtained for the mercury analogous to equations 2–5. Substituting in the Duhem equation, d log $(a_1/N_1) = -(N_2/N_1)$ d log (a_2/N_2), the value of log (a_2/N_2) given by equation (2), and integrating we obtain the activity of the mercury as a function of N_2 and T. The integration constant is zero inasmuch as at zero concentration of potassium log a_1/N_1 equals zero. In this way equation (6) is obtained

$$\log \frac{a_1}{N_1} = -\frac{2446}{T^{0.77700}} \left\{ \frac{N_2^2}{2} + \frac{N_2^3}{3} + \frac{N_2^4}{4} + 13{,}721 \left(\frac{N_2^5}{5} + \frac{N_2^6}{6} \ldots \right) \right\} \qquad (6)$$

Following the method just employed for potassium three more equations may be derived for mercury.

$$\bar{F}_1 = 4.5739 \left[T \log_{10} N_1 - 2446 T^{0.22300} \left\{ \frac{N_2^2}{2} + \frac{N_2^3}{3} + \frac{N_2^4}{4} + 13{,}721 \left(\frac{N_2^5}{5} + \frac{N_2^6}{6} \ldots \right) \right\} \right] \qquad (7)$$

$$\bar{S}_1 = -4.5739 \left[\log_{10} N_1 - 545 T^{-0.77700} \left\{ \frac{N_2^2}{2} + \frac{N_2^3}{3} + \frac{N_2^4}{4} + 13{,}721 \left(\frac{N_2^5}{5} + \frac{N_2^6}{6} \ldots \right) \right\} \right] \qquad (8)$$

$$\bar{H}_1 = -8693 T^{0.223} \left\{ \frac{N_2^2}{2} + \frac{N_2^3}{3} + \frac{N_2^4}{4} + 13{,}721 \left(\frac{N_2^5}{5} + \frac{N_2^6}{6} \ldots \right) \right\} \qquad (9)$$

The Solid Phase

We turn now to a discussion of the data involving amalgams in which a solid phase is present. These data are recorded in the second column of Table II. The plot of these measurements is shown by the steep curve in Fig. 3. The equation for this curve is

$$\Delta E = 0.00533 + 1.5153 \times 10^{-3}(T - 273.2) + 6.94 \times 10^{-6}(T - 273.2)^2 \qquad (10)$$

On the same plot are shown the curves for single-phase amalgams, points to the left of the curve of equation (10) representing supercooled amalgams. These five curves were drawn with the aid of equation (1). Each of the five curves thus represents an amalgam of known concentration. Each intersection with the two-phase amalgam curve gives a concentration and a temperature. Thus by simultaneous solution of equations (1) and (10) the data of Table IV for the solubility of potassium in mercury have been obtained. These data are shown graphically in Fig. 4. The equation for this curve is

$$x = 0.00252 + 8.12 \times 10^{-5}(T - 273.2) + 8.40 \times 10^{-7}(T - 273.2)^2$$

in which "x" is the weight fraction of potassium in the saturated amalgam.

TABLE IV

THE SOLUBILITY OF POTASSIUM IN MERCURY

Values of the mole fraction are obtained by simultaneous solution of equations (1) and (10)

Temp., °C.	Mole fraction	Weight fraction	Temp., °C.	Mole fraction	Weight fraction
0	0.01271	0.00250	18.82	0.02191	0.00435
6.15	.01544	.00305	23.09	.02428	.00483
14.35	.01951	.00386	25.00	.02536	.00505
15.00	.01986	.00393	26.79	.02638	.00525

The free energy and heat of formation of the solid phase may also be calculated from these data. Smith and Bennett[7] have shown that the solid phase in equilibrium with dilute potassium amalgams has the composition represented by KHg_{12}. At equilibrium the free energy of solution of this compound in the liquid is zero. The free energy of formation of the compound is, therefore, just the sum of the relative partial molal free energies of the elements in the liquid. $\Delta F = 12\bar{F}_1 + \bar{F}_2$. $\bar{F}_1$ is found from equation (7) to be -29.43 calories and $\bar{F}_2$ is found from equation (3) to be $-23,077$ calories. Therefore ΔF for the formation of solid KHg_{12} from the elements is $-23,430$ calories.

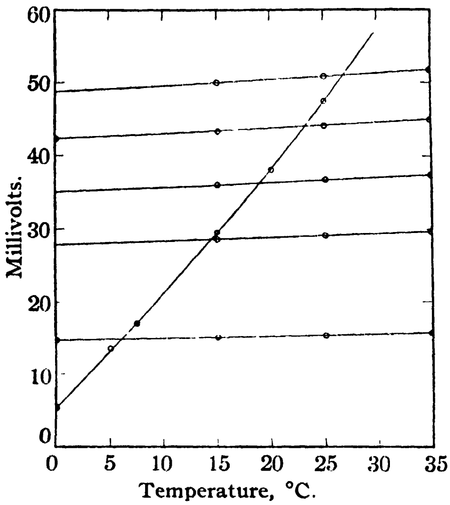

Fig. 3.—The e. m. f. of two-phase amalgams against amalgam VI. Also corresponding values for single phase amalgams against amalgam VI.

Under the restriction that the solution is to remain saturated F_1 and F_2 are functions of the temperature alone and

$$\frac{d\Delta F}{dT} = 12\frac{d\bar{F}_1}{dT} + \frac{d\bar{F}_2}{dT}, \text{ and}$$

$$\frac{d\bar{F}_1}{dT} = \frac{\partial \bar{F}_1}{\partial T} + \frac{\partial \bar{F}_1}{\partial N_2}\frac{dN_2}{dx}\frac{dx}{dT} = -\bar{S}_1 + \frac{\partial \bar{F}_1}{\partial N_2}\frac{dN_2}{dx}\frac{dx}{dT}$$

From equation (8) $\bar{S}_1$ is 0.6166, from equation (7) $\partial\bar{F}_1/\partial N_2$ is -1877 calories per mole per mole fraction unit. From the definition of the mole fraction dN_2/dx is 4.9235 when N_2 is 0.02536. From equation (11) dx/dT is 0.0001232 at 25°. Consequently $d\bar{F}_1/dT = -1.2002$ calories per mole.

The easiest way to obtain $d\bar{F}_2/dT$ is to go back to the e. m. f. data. We may write

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[7] Smith and Bennett, THIS JOURNAL, 32, 624 (1910).

$$\frac{d\bar{F}_2}{dT} = -23{,}065\left(\frac{dE_1}{dT} + \frac{dE_2}{dT}\right)$$

in which E_1 is the e. m. f. measured by Lewis and Keyes, potassium to our amalgam VI, and E_2 is the e. m. f. of the saturated amalgam to this same amalgam VI. After the slight correction for the pressure effect dE_1/dT is -0.000273. Equation (10) on differentiation gives dE_2/dT as -0.001862. Hence $d\bar{F}_2/dT$ is the sum of these two values multiplied by 23,065 or 49.24 calories. Hence $d\Delta F/dT = -\Delta S = 49.23 - 14.49 = 34.84$ calories per mole per degree. From the relation $\Delta H = \Delta F + T\Delta S$ one finds that $\Delta H = -33{,}819 \pm 30$ calories per mole.

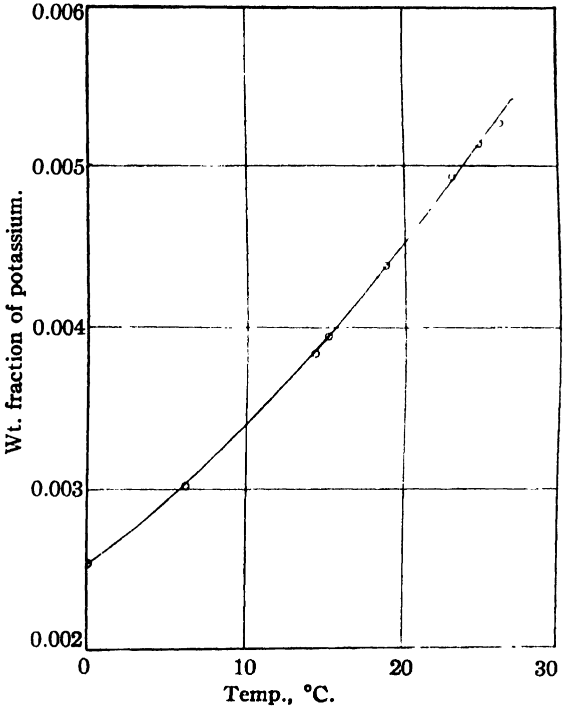

Fig. 4.—The solubility of potassium in mercury.

These figures enable one to calculate the heat of solution of the compound in the saturated solution. Equations (5) and (9) enable one to calculate the heat of formation of the compound in solution and give a value of −25,705 calories. Hence the heat of solution of the compound in saturated solution is 8114 calories per mole. Finally, equation (5) gives the heat of solution of potassium at infinite dilution as −26,150 calories. Hence the heat of solution of the compound in a large amount of mercury is 7669. Finally the relative partial molal heat content of the compound in the saturated solution referred to the infinitely dilute solution as the standard state is −445 calories.

Discussion of Results

In discussing the extreme deviations from Raoult's law exhibited by potassium amalgams we will approach the subject in two quite different ways. We will discuss first the significance of compound formation and later some inferences to be drawn from the thermodynamic data.

One may start by assuming that there are compounds in the liquid phase which have the same formulas as the solid phases indicated by the phase diagram. One may also assume that these compounds are only slightly dissociated in the liquid phase and that the various molecular species obey Raoult's law. This last assumption is only a first approximation. It has previously been shown that with the aid of these assumptions one may account for the vapor pressure of mercury and for the activity of sodium in dilute sodium amalgams.[8] The agreement of the calculated vapor pressures with the experimental values is not very good if one uses only the formulas of definitely established solid compounds. There is some uncertainty, however, as to just how many of these compounds exist and there is no proof that the same compounds exist in solution. By assuming additional compounds in solution one can obtain excellent agreement with the experimental data. This treatment does not prove that these compounds exist but indicates that the experimental facts are not incompatible with compound formation. The experimental data of Richards and Conant which were used in the above computation are not of sufficient accuracy in the most dilute range of concentration to enable one to say whether the hypothesis of compound formation accounted well for the data or not. On a plot such as that in Fig. 2 the data of Richards and Conant showed a decided dropping off in the range of low concentration. A curve obtained by assuming only one compound, $NaHg_{16}$, on the other hand, showed a slight flattening out in the range of small concentration. The data obtained in this research on potassium, on the other hand, show not the slightest deviation from a straight line in the range of small concentration. Our most dilute amalgam was about one-tenth the concentration of the most dilute amalgam of Richards and Conant. One could doubtless obtain a curve which would fit the experimental data by assuming a compound containing still a larger percentage of mercury. Such a procedure at present, however, seems quite useless. We have no reason for thinking that the various molecular species obey Raoult's law to anything more than a first approximation, and until we can calculate or determine these deviations it is impossible to push the hypothesis of compound formation farther. At present it is only possible to say that a large part of the deviation from Raoult's law exhibited by amalgams of the alkali

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(8) Bent and Hildebrand, THIS JOURNAL, 49, 3011 (1927).

metals may be accounted for by assuming slightly dissociated compounds in the liquid phase.

Turning now to the partial molal quantities given in Table III we see some interesting facts. All of these partial molal quantities change very little with changing temperature. This result is perhaps due in part to the limited amount of data on cells containing potassium. Thus Lewis and Keyes made measurements at but two temperatures in order to obtain the temperature coefficient of the e. m. f. If we assume that d^2E/dT^2 is zero we are probably not introducing a very serious error in our computations since the first derivative is not large. However, it is just this assumption which causes the partial molal entropy and heat of potassium to be essentially constant. Since $\bar{F}_2$ is large it follows that it will not change much with the temperature but will change more than the heat or entropy as may be seen from the equation $\bar{F}_2 = \bar{H}_2 - T\bar{S}_2$. Multiplying $\bar{S}_2$ by T causes this product to change with the temperature even when $\bar{S}_2$ is constant. Turning now to the curves in Fig. 2 we note that their displacement with changing temperature is, therefore, due chiefly to the T coming into the equation $\bar{F}_2 = RT \ln a_2$.

The effect of temperature on deviations from Raoult's law has been discussed by Shibata and Oda[9] in a recent article in which they come to the conclusion that at 300–400° these amalgams become ideal solutions! This seems an extraordinary conclusion based on the extrapolation of an equation which is essentially empirical. Thus they find that the slope of their curves, when plotting data as in Fig. 2, is decreasing as the temperature rises. Assuming that the decrease in slope is a linear function of the temperature they arrive at a comparatively low temperature at which amalgams should become ideal solutions. In a similar manner if we take equation (2) which expresses our results within the error of our experiments we find that the coefficient of N_2 does not become zero until the temperature becomes infinite. Neither of these conclusions can be justified. In both cases empirical equations are being extrapolated far beyond the range of temperature for which they have been found to hold. This point will be discussed further in the next paragraph.

Another significant observation is that the partial molal entropy of the potassium is negative. For an ideal solution it would be positive and equal to $-R \ln N_2$. This rather large negative value more than offsets the small positive partial molal entropy for mercury with the result that there is actually a decrease in entropy in forming all but the most dilute amalgams from the elements. This clearly indicates that the amalgam does not have the random distribution of atoms that one would expect for an ideal solution but that some process, such as compound formation, has taken place to decrease the entropy.

[9] Shibata and Oda, *J. Chem. Soc. Japan*, **52**, 352–364 (1931).

One must conclude from these facts that the various physical theories of binary mixtures are not applicable to potassium amalgams.[10] Not only is the entropy very much less than that which is assumed by the physical theories but there is a large contraction during the formation of the amalgam. This latter fact prevents one from calculating surface fractions or volume fractions as is done by Langmuir and Scatchard. However, these values would differ little from the mole fraction and could not be of significance in such dilute solutions. In view of the fact that potassium amalgams are so decidedly irregular, using the definition of regular given by Hildebrand, it is perhaps surprising that the data may be represented by the same equations as have been derived by the various physical theories. It is not apparent at first glance that this is so. However, equations (2) and (6) reduce to much simpler equations at constant temperature if one is not interested in an accuracy of more than a few tenths of a per cent. Equation (2) then assumes the familiar form $\log a_2/N_2 = \beta N_2$ and equation (6) becomes $\log a_1/N_1 = {}^1/_2\beta N_2^2$. At higher concentrations, which unfortunately cannot be secured at room temperature on account of the appearance of a solid phase, doubtless such simple equations could not be used. Perhaps the most significant inference which one may draw from these facts is that considerable caution is necessary in drawing any conclusion as to the correctness of a theory from the fact that the data agree with the results of the theory. Thus potassium amalgams very definitely do not conform to the assumptions of the theory of Heitler, yet they may be described quite well by the form of equation obtained by him.

In spite of the very "irregular" nature of potassium amalgams, a rather simple picture of the system is still possible. We may sum up the facts which we now have as follows. There are large forces acting between mercury and potassium atoms ($\overline{H}_2$ is large and negative). The forces as a first approximation are not affected by a rise in temperature. The organization or arrangement of atoms in the amalgam is also not affected, as a first approximation, by a change in temperature ($\overline{S}_1$ and $\overline{S}_2$ change little with temperature). The activity of potassium, however, is increased to a marked degree by increasing the temperature. This may be considered to be due to the fact that the heat of vaporization of potassium from an amalgam is much larger (due to $\overline{H}_2$ being large and negative) than from the pure metal and hence the vapor pressure increases much more rapidly from the amalgam than it does from the pure metal.

Finally, we might point out that some of the amalgams used in this investigation were kept for as much as six months. During this time there was apparently no change in the activity of the alkali metal. Some of the cells were studied for many weeks and also showed no change in e. m. f. with either variation in temperature or with the lapse of time. If these

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(10) Scatchard, *Chem. Rev.*, **8**, 321 (1931).

amalgams were colloidal, as suggested by Paranjpe and Joshi,[11] one would not expect such reproducibility.

Summary

1. Galvanic cells have been studied in which the reaction is the transfer of potassium from an amalgam of higher concentration to one of lower concentration. The e. m. f. of such cells has been determined as a function of temperature and concentration of the amalgam.

2. The partial molal free energy, heat and entropy of the potassium and mercury have been calculated.

3. The solubility of potassium in mercury has been determined from 0–50°.

4. The free energy and heat of formation of the compound KHg_{12} and the heat of solution of this compound have been determined.

5. The significance of these data is discussed.

[11] Paranjpe and Joshi, *J. Phys. Chem.*, **36**, 2474 (1932); Bent, *ibid*, **37**, 431 (1933).

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 1, 1933
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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Kinetics of Gas Explosions. IV. Ozone Explosions Induced by Hydrogen[1,2]

BY BERNARD LEWIS[3]

Introduction

The influence of hydrogen on the thermal decomposition of ozone was studied by Belton, Griffith and McKeown.[4] They found that two reactions occurred simultaneously, the decomposition of ozone and the formation of water. The addition of hydrogen to ozone increased the specific rate of ozone decomposition. For example, their bimolecular velocity constant of ozone decomposition increased sixfold when 156 mm. of hydrogen was added to a mixture of 70 mm. of ozone and 650 mm. of oxygen. The velocity constant for the formation of water by the assumed reaction $H_2 + O_3 = H_2O + O_2$ increased less rapidly, it being only threefold on increasing the hydrogen pressure from 33 mm. to 156 mm. in a similar mixture. The amount of hydrogen converted to water was small in comparison with the ozone decomposed. The available data published by these authors indicate that the percentage of hydrogen converted (measured when most of the ozone had decomposed) depends much more on the ozone concentration than on the hydrogen concentration. It increases

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Parts I, II, III, with W. Feitknecht, THIS JOURNAL, **53**, 2910 (1931); **54**, 1784, 3185 (1932).

[3] Physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[4] Belton, Griffith and McKeown, *J. Chem. Soc.*, **128**, 3153 (1926).

a little with increasing initial ozone concentration. The effect of increasing the temperature is to increase the percentage conversion of hydrogen. Thus at 78° it amounted to about 7% in a mixture 38 mm. of ozone, 230 mm. of hydrogen, 450 mm. of oxygen, while at 100° it was about 9.5% in a mixture 35 mm. of ozone, 145 mm. of hydrogen and 500 mm. of oxygen. Our own results agree reasonably well with these values, the percentage conversion of hydrogen being about 7 to 8% in a mixture 50 mm. of ozone, 90 mm. of hydrogen and about 3 mm. of oxygen at 85°.

It is the purpose of this paper to present some rather striking results which indicate that the reaction mechanism of the process is much more complicated than Belton, Griffith and McKeown assumed, that the enhanced rate of ozone decomposition in the presence of hydrogen is due to the initiation of a chain reaction through the medium of hydrogen atoms.

Apparatus and Procedure

Details of the experimental arrangement are given in Part I of this series. In these experiments pure ozone (98–99%) was used. Electrolytic hydrogen was purified by passing it through a layer of charcoal cooled to liquid air temperature. The rise in pressure due to reaction was measured with a quartz spiral manometer. The method of preparing the gases ensured such a purity that the ozone alone or ozone in the presence of hydrogen was extremely stable at room temperatures, there being no appreciable rise in pressure over a period of several hours. Spherical glass reaction vessels of about 200 cc. capacity were used.

The formation of water involves no pressure change, but since the amount of hydrogen converted is small, the rise in pressure represents, as a first approximation, the ozone decomposed.

Results

It was found that the addition of hydrogen to pure ozone at 85° has an enormous effect on the rate at which the pressure increases. For a given ozone pressure (50 mm.), $\Delta p/\Delta t$ is practically proportional to the hydrogen pressure, for relatively low pressures of the latter. Above 50 mm. of hydrogen the rate increases very rapidly, the normal rate of ozone decomposition increasing by hundreds of times for about 70–75 mm. of hydrogen. At about 80 mm. of hydrogen an explosion occurs. Table I shows the time required for the pressure to increase the first 8 mm. for increasing amounts of hydrogen added to 50 mm. of ozone.

TABLE I

INFLUENCE OF HYDROGEN ON THE RATE OF PRESSURE INCREASE (OZONE PRESSURE, 50 MM.)

Pressure of hydrogen, mm.	None	10.1	30.5	50.0	80.0
Time in minutes for Δp = 8 mm.	120	29	11	5.25	Explosion

The pressure of hydrogen necessary to cause explosion increases as the pressure of ozone decreases. Thus, for 40 mm. of ozone the pressure of hydrogen necessary to explode the mixture at 85° is 100 mm.; for 50 mm.

of ozone it is 80 mm. Presumably there is some lower limit of ozone pressure and hydrogen pressure below which no explosion is possible.

A very interesting effect was observed. If the reaction rate is measured for several successive runs using a similar but fresh mixture after evacuating for about five minutes between each run, the reaction rate increases in each succeeding experiment. With each experiment the reaction vessel becomes more active. If a mixture just above the explosion limit is admitted to an inactive vessel, it does not explode until several such experiments are carried out in the vessel. If the mixture is below the explosion limit the rate reaches a constant maximum value. This effect is illustrated in the following table in which the time is given for Δp to reach a certain value for several runs starting in an inactive vessel with a mixture below the explosion limit.

TABLE II

EFFECT OF PREVIOUS EXPERIMENTS ON THE RATE OF PRESSURE INCREASE

Ozone pressure, 50 mm. Hydrogen pressure, 50 mm.

Experiment	1	2	3	4
Time in minutes for Δp = 10.5 mm.	13	8.2	7.3	7.2

The activity acquired by the vessel after the above treatment lasts for several hours, and even after twenty hours the vessel still shows small evidences of it. The vessel can be deactivated by heating and pumping with a mercury vapor pump for some time.

It is believed that the increased activity of the vessel is due to the formation during the reaction of some substance which is adsorbed on the wall and which facilitates the process. This substance may be water or some active radical or atom. While it was found, in agreement with Warburg,[5] that the presence of water increases the rate of decomposition of ozone, this effect is very much smaller than that encountered in the above phenomenon. The following experiment shows that water is not the cause of the enhanced activity of the vessel. A vessel was activated to the explosion point by running several experiments with a mixture 50 mm. of ozone and 90 mm. of hydrogen. During an explosion all the hydrogen is burned to water. The products of the explosion were allowed to remain in the vessel for about thirty hours, after which they were pumped out quickly, leaving a layer of water on the wall. If the activity were due to water, a similar explosive mixture might be expected to explode. Instead, a reaction occurred comparable in rate with that to be expected in an inactive vessel.

It was suspected that the cause of the activity was the adsorption on the walls of hydrogen atoms formed during the reaction. This was shown to be very probable by the following set of experiments. The inactive vessel was pumped out for some time, hydrogen admitted to a pressure of about

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(5) Warburg, *Sitzb. preuss. Akad. Wiss.*, 644 (1913).

0.5 mm. to 1 mm. and a discharge passed through the gas for about fifteen minutes at room temperature. A mixture of 50 mm. of ozone, 80 mm. of hydrogen, was admitted to the vessel, which was still at room temperature. The reaction which occurred was negligibly small. (Similarly, the reaction is inappreciable at room temperature in a very active vessel, made active by first running several experiments at 85°.) The vessel was pumped out, heated to 85°, and three hours later received a similar mixture. The mixture exploded promptly. Thus, even after this time the vessel was sufficiently active to explode the mixture, which without the previous sparking treatment would have reacted non-explosively. It may be concluded that hydrogen atoms formed during the discharge, likewise during a reaction, are adsorbed on the wall in some active form which is responsible for the enhanced activity of the vessel.

That the activity is not attributable to oxygen atoms is shown by the fact that the explosion of pure ozone alone (ignition by local heating with a flame) in an inactive vessel, during which many oxygen atoms are formed, does not alter the activity of the vessel appreciably.

Discussion

It is proposed that the adsorbed active hydrogen facilitates the starting at the walls of reaction chains which then spread out into the gas phase.[6] The following mechanism may be suggested as being consistent with the known facts.

At the outset, a certain number of oxygen atoms are formed during the normal thermal decomposition of ozone.

$$O_3 \longrightarrow O_2 + O \qquad (1)$$

Hydrogen atoms may be generated as follows

$$O + H_2 = OH + H\ (+\ 1\ \text{Kcal.}) \qquad (2)$$

The velocity of formation of hydrogen atoms for a given ozone concentration would be proportional to the hydrogen concentration. The hydrogen atoms now react with ozone relatively easily giving rise to active OH radicals which in turn react with ozone, regenerating hydrogen atoms; *i. e.*

$$H + O_3 = OH^* + O_2^*\ (+\ 78\ \text{Kcal.}) \qquad (3)$$

$$OH^* + O_3 = 2O_2 + H\ (-10\ \text{Kcal.}) \qquad (4)$$

where the * indicates an energy-rich molecule. The initial presence on the walls of active hydrogen (supposedly behaving as atomic hydrogen), as in the activated vessel described above, would enable reactions 3 and 4 to proceed therefrom without waiting for the hydrogen concentration to build up through reaction 2. If a sufficient number of reaction 3 is started in unit time the gas will heat up and accelerate all four reactions.

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(6) A similar phenomenon was reported by Farkas, Haber and Harteck [*Z. Elektrochem.*, **36**, 711 (1930)] in the explosion of hydrogen and oxygen. If the vessel had been prepared by exploding a mixture of hydrogen and oxygen with a spark at 420°, a second and similar mixture admitted to the evacuated vessel a minute or two later exploded spontaneously. This effect was attributed to the adsorption on the walls of an active product, presumably hydrogen atoms.

Under suitable conditions an explosion results. More hydrogen atoms may be formed by means of the following step coupled with reaction 2.

$$O_2^* + O_3 = 2O_2 + O\ (-25\ \text{Kcal.}) \qquad (5)$$

The oxygen atoms may also decompose ozone, giving rise to another chain of reactions, the nature of which is not entirely clear[7] but which may be written for the time being simply as

$$O + O_3 = 2O_2^*\ (+93\ \text{Kcal.}) \qquad (6)$$
$$O_2^* + O_3 = 2O_2 + O\ (-25\ \text{Kcal.}) \qquad (7)$$

The mechanism of the formation of water from hydrogen and oxygen is still in a state of uncertainty. So far these experiments throw no additional light on the subject. The Bonhoeffer–Haber[8] mechanism would indicate the following step

$$OH + H_2 = H_2O + H\ (+14\ \text{Kcal.}) \qquad (8)$$

The efficiency of this reaction at 85° is quite low,[9] but with the energy attached to the OH^* radical emerging from reaction 3, reaction 8 would be expected to occur fairly frequently, although OH radicals from reaction 2 would be comparatively ineffective. With reaction 3 removing hydrogen atoms rather easily and the existence of a competition for OH between reactions 4 and 8, it should be difficult to complete the Bonhoeffer–Haber chain, especially while the ozone concentration is appreciable. It is apparent that the amount of hydrogen converted to water should be low in comparison with the ozone decomposed, which is in agreement with the experiment. Of course, the reaction

$$O_2^* + H_2 = H_2O + O\ (-1\ \text{Kcal.}) \qquad (9)$$

is not impossible. A quantitative study of the amount of hydrogen and ozone converted from point to point in a given run might contribute valuable information toward elucidating the mechanism of the burning of hydrogen. This involves elaborate technique and has not been attempted so far.

If the formation of water occurs through the medium of hydrogen peroxide, it might be argued that the enhanced decomposition of ozone is also due to this molecule. It is, however, difficult to understand how a regenerative chain could be set up under these conditions to account for the high rate of ozone decomposition. The point could be tested experimentally by mixing hydrogen peroxide and ozone and if a reaction occurs determining whether more ozone decomposes than corresponds to the equation $O_3 + H_2O_2 = H_2O + 2O_2$.

Summary

Experiments were carried out at 85° to determine the influence of hydrogen on the thermal decomposition of ozone. With addition of hydrogen, the rate of decomposition increases enormously up to the point of

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(7) Bernard Lewis, *J. Phys. Chem.*, **37**, 533 (1933).

(8) Bonhoeffer and Haber, *ibid.*, **137A**, 227 (1928); Haber, *Z. angew. Chem.*, **42**, 745 (1930).

(9) Von Elbe and Lewis, THIS JOURNAL, **54**, 552 (1932).

explosion, which occurs under suitable pressure conditions. Thus 50 mm. of ozone requires 80 mm. of hydrogen, while 40 mm. of ozone requires 100 mm. of hydrogen to cause the mixture to explode at 85°. The amount of hydrogen converted to water in the non-explosive reaction is only a fraction of the ozone decomposed.

An ordinary glass vessel becomes activated during the course of a reaction. In each succeeding reaction the vessel exhibits increased activity. The criterion for activity is the rate of reaction. Thus, an explosive limit mixture will not explode until several runs are carried out in the vessel first, while with a non-explosive mixture the reaction rate increases in each succeeding experiment until a constant value is reached. The activity lasts for several hours. Experiments were performed which indicate that the activity is due to the formation, during the reaction, of hydrogen atoms which are adsorbed on the walls. A mechanism of the process is suggested by which hydrogen atoms take part in a chain of reactions accounting for the bulk of the enhanced decomposition of ozone, *i. e.*, $H + O_3 = OH^* + O_2^*$ and $OH^* + O_3 = 2O_2 + H$, where * represents a molecule rich in energy.

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A Note on the Heat of Sorption of Water Vapor by Massive Gold

BY ELLIOTT PIERCE BARRETT

A paper by Barry and Barrett[1] describes the methods used and the results obtained in a study of the heat of sorption of water vapor by massive gold in a saturated atmosphere. It is the purpose of this communication to point out that the relationship between heat of sorption and weight of vapor sorbed obtained from that investigation is similar to that found by other investigators working with quite different systems.

In the joint paper to which reference has been made, it was shown that for water vapor and gold, the integral heat of sorption, H, at any time, t, measured from the beginning of sorption, is given by the relation

$$\log H = a - b/t^c \qquad (1)$$

where a, b and c are empirical constants. An analogous equation

$$\log W = a' - b'/t^{c'} \qquad (2)$$

was shown to describe the increment in weight, W, of the gold which accompanied the liberation of heat and which was assumed to measure the quantity of water vapor sorbed by the gold.

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[1] Barry and Barrett, THIS JOURNAL, 55, 3088 (1933).

Since it was also found that c and c' were identical to well within the limits of experimental error, equations 1 and 2 can be combined and the quantity t eliminated from them so that H is expressed directly as a function of W by the relationship

$$H = mW^n \tag{3}$$

which is identical in form with the equation $q = ax^b$ found by Lamb and Coolidge[2] to describe the relationship between heat of sorption and weight sorbed in the case of eleven organic vapors sorbed by steam-activated coconut charcoal.

The constants m and n of equation 3 have been evaluated from the experimental data and a comparison between the integral heat of sorption as measured and as calculated from equation 3 is made in Table I.

TABLE I

COMPARISON OF OBSERVED VALUES OF INTEGRAL HEAT OF SORPTION WITH THOSE CALCULATED FROM THE EQUATION $H = 13.3W^{0.340}$

Time, hours	Wt. sorbed per sq. cm. in grams × 10^6	Obs. heat per sq. cm. in milli-calories	Calcd. heat per sq. cm. in milli-calories	Time, hours	Wt. sorbed per sq. cm. in grams × 10^6	Obs. heat per sq. cm. in milli-calories	Calcd. heat per sq. cm. in milli-calories
0.5	1.08	13.7	13.7	4.0	6.54	25.2[a]	..
1.0	2.34	17.8	17.8	4.5	6.92	25.7	25.7
1.5	3.32	20.1	20.0	5.0	7.25	26.2	26.1
2.0	4.21	21.7[a]	..	5.5	7.57	26.6	26.4
2.5	4.86	22.9	22.8	6.0	7.95	27.0	26.9
3.0	5.51	23.5	23.8	Infinity	24.85[b]	39.7[c]	39.7
3.5	6.03	24.6	24.5				

[a] Used to evaluate m and n. [b] Calculated from equation 2. [c] Calculated from equation 1.

It is interesting to compare these results with the data of Lamb and Coolidge, to which reference has been made above. Their values of n for the several vapors vary from 0.900 to 0.959, indicating that the change in the differential heat of sorption with increasing sorption is small. The relatively small value of n which appears in Table I shows clearly that, for water vapor and gold, the differential heat of sorption changes rapidly with increasing sorption for small values of W and that, as the weight sorbed increases, the value of the differential heat changes more slowly.

Since the actual measurements of the heat of sorption of water vapor by gold only covered a period of six hours, measured from the beginning of sorption, and since it is impractical to make calorimetric measurements over a sufficient length of time to determine even three-quarters of the integral sorption heat at equilibrium, it becomes important to form some estimate of the reliability of equation 3, when it is used to calculate values of H beyond the experimental time limit. Such an estimate can be made readily since the experimental conditions were such that it was thermodynamically necessary for the differential heat of sorption to approach the heat of evaporation of water as the system approached equilibrium.

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[2] Lamb and Coolidge, THIS JOURNAL, 42, 1146 (1920).

Extrapolation, by means of equation 2, gives 24.85×10^{-6} g. as the weight of water vapor sorbed per square centimeter of gold at equilibrium. Differentiation of equation 3 gives

$$dH/dW = 4.52/W^{0.66} \tag{4}$$

Substitution of 24.85 in equation 4 gives 543 calories per gram as the heat of evaporation of water, which value is in error by 6%. Since the estimated error of measurement is 5%, it may be said that equation 3 describes the phenomenon with reasonable accuracy.

It is apparent from the form of equation 4 that, as W approaches zero, the differential heat of sorption approaches infinity. There are two possible interpretations of this observation. One is that the equation does not hold for very small values of W, although it does describe the phenomenon through the experimental range and, by deductive inference, out to infinite time. The other is that the equation does have significance even though W be an infinitesimal. The rational consequence of the second assumption is not that the first molecule of vapor sorbed liberates infinite heat but, simply, that it is impossible to remove the last molecule of water from a gold surface.

In the paper by Barry and Barrett[1] it was suggested that the exceedingly protracted nature of the phenomenon was probably due to diffusion of water vapor into the massive gold; so that, although sorption upon the exposed surface was extremely rapid, being, in all probability a true adsorption, the nature of the initial process was masked, since diffusion of adsorbed water into the gold would unsaturate the surface, thereby necessitating the adsorption of further water vapor in order to establish equilibrium between the gold surface and the saturated atmosphere.

Recently W. R. Ham, Professor of Physics at the Pennsylvania State College, has interested himself in this phase of the problem and has very kindly communicated to the writer the results of his preliminary measurements of the rate of diffusion of water vapor through gold. Ham has found that the diffusion at 400° and higher temperatures is readily measurable and although diffusion at these temperatures cannot be regarded as proof that the phenomenon occurs at room temperature, it does lend credibility to the original hypothesis.

It is possible to calculate from Ham's data the differential heat of sorption for very low relative humidities. His average value for measurements of about two hours' duration is 2500 calories per gram. The average heat of sorption found by Barry and Barrett during the first two hours of measurement was 5100 calories per gram. In view of the different working conditions the agreement in order of magnitude is gratifying.

Summary

It is shown that the integral heat of sorption of water vapor by massive gold is described by the equation $H = mW^n$, which is identical in form with the equation of Lamb and Coolidge for the sorption of organic vapors by charcoal.

The consequences of this observation are discussed and a possible mechanism by which the sorption occurs is considered.

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Hydrides of Boron. II. The Preparation of B_5H_{11}: Its Thermal Decomposition and Reaction with Hydrogen

BY ANTON B. BURG AND H. I. SCHLESINGER

The development of a rapid and efficient method of preparing diborane (B_2H_6)[1] has made desirable the finding of efficient methods of preparing from it the less volatile hydrides of boron. Our experiments in this direction have led to the development of a satisfactory procedure for the preparation of the hydride B_5H_{11} and to a study of the properties of this hitherto little known substance. These investigations, in turn, have made possible improvements in the preparation of B_5H_9 from diborane, and have indicated a method by which useful quantities of the tetraborane (B_4H_{10}) may be prepared without recourse to the less efficient procedures involving the use of boron alloys.

When the pentaborane, B_5H_{11}, is heated at 100° without addition of excess of hydrogen, the first detectable effect is the production of small quantities of hydrogen, diborane, tetraborane and traces of a slightly volatile substance which seems to be an octaborane. Non-volatile solids appear soon afterward, but the formation of the latter seems to be inhibited to a certain extent by the accumulation of hydrogen. Within an hour the system, involving the substances named above, seems to reach a condition of equilibrium which is slowly shifted by the very gradual formation of B_5H_9,[2] traces of $B_{10}H_{14}$ and the non-volatile solids.

The indications that reversible changes are involved in these reactions led to the study of the effect of a high initial concentration of hydrogen. Under these conditions, the first reaction proceeds almost entirely according to the equation $2B_5H_{11} + 2H_2 \rightleftarrows 2B_4H_{10} + B_2H_6$. The tetraborane reacts further, but more slowly, mainly according to the equation $B_4H_{10} +$

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(1) Schlesinger and Burg, THIS JOURNAL, 53, 4321 (1931).

(2) Because of the existence of the two substances B_5H_9 and B_5H_{11} which cannot be satisfactorily named till more is known about their structure, we shall refer to them only by formula. The term pentaborane will hereinafter be used only to refer to mixtures of the two.

$H_2 \rightleftarrows 2B_2H_6$, until the whole system reaches a state of equilibrium in which the concentrations of B_4H_{10} and B_5H_{11} are low. Here, also, further heating results in the formation of B_5H_9, $B_{10}H_{14}$ and the non-volatile solids; the last are formed much more slowly and are much lighter in color than those produced in the absence of hydrogen.[3]

Although the presence of hydrogen inhibits the formation of the non-volatile hydrides, the latter do not themselves react with hydrogen to reproduce the volatile substance. The effect of the hydrogen is, therefore, best explained by assuming that it decreases the concentration of slightly volatile products (among which may be the octaborane mentioned above) which yield the solids by a secondary reaction.

On the other hand, hydrogen seems not to interfere at all with the formation of $B_{10}H_{14}$ and B_5H_9. For this reason it has been found possible to improve the yields of the latter by adding a high concentration of hydrogen to the reaction mixture before heating it.

The thermal decomposition of B_5H_{11} and its reaction with hydrogen are most easily understood by supposing that the structure of this substance is an open chain, whose most probable mode of decomposition is a break at one end. This picture accounts very well for the reaction with hydrogen, which produces one molecule of tetraborane from each molecule of pentaborane used up. This reaction may be an addition of hydrogen to the tetraboryl and monoboryl radicals produced by the breakdown of the five-atomic chain. The same assumption would account for the formation of an octaborane in the absence of hydrogen, under which conditions some of the tetraboryl radicals might unite to form eight-atomic chains.

Whatever the mechanism, the reaction of B_5H_{11} with hydrogen gives us an efficient means of preparing tetraborane. The development of a convenient technique for carrying on this reaction on a large scale should make this substance considerably more easily available than it has been before. A flow method should be suitable for the purpose.

Stock and Siecke[4] have given reasons for believing in the existence of a third pentaborane, distinct from B_5H_9 and B_5H_{11}. We have been unable to find any evidence in support of this assumption. On the contrary, our observations of the behavior of B_5H_{11}, whether alone or mixed with a large proportion of B_5H_9, agree perfectly with the observations of Stock and Siecke on the behavior of "$B_5H_{>9}$" in its mixtures with B_5H_9. It is reasonable to believe that "$B_5H_{>9}$" and B_5H_{11} are identical. At the same time we must recognize that our observations on B_5H_{11} do not agree perfectly with those of Stock and Siecke, who were led to suppose that B_5H_{11} is an intermediate in the formation of $B_{10}H_{14}$. It seems best to ascribe the discrepancies to differences in the quantities and kinds of impurities, rather than to any difference in the substance itself.

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[3] This effect of hydrogen makes it useful as a preservative of the volatile hydrides. A sample of diborane at room temperature produces non-volatile solids amounting to 10% of the sample in one year. In the presence of an equal volume of hydrogen, the loss of volatile substances is scarcely observable.

[4] Stock and Siecke, *Ber.*, **57B**, 562 (1924).

The Preparation of B_5H_{11}

I. At Room Temperature.—In our first experiments we obtained B_5H_{11} by allowing samples of diborane to stand for months at a time in sealed bulbs at room temperature (20–30°). The material in each bulb was introduced into the vacuum apparatus by means of the tube-opener[5] and the products were separated by the method of fractional condensation (B_5H_{11} trapped at $-85°$, B_4H_{10} at $-124°$ and B_2H_6 condensed at $-190°$). The results are shown in Table I.

TABLE I

Conditions			Products (cc. gas)			Results	
Vol. of B_2H_6, cc.	Vol. of bulb, cc.	Time, months	Hydrogen	B_4H_{10}	B_5H_{11}	% Reaction of B_2H_6	% Yield B_5H_{11} + B_4H_{10}, %
1050	3400	0.5	..	...	2.5	0.6	100
447	1050	3.3	37.6	1.4	8.3	8.5	80
495	600	3.3	37.0	1.4	8.3	7.7	80
380	1050	13.5	88.8	6.8	8.0	21.8	40
1080	1100	4.0	111.0	13.0	20.6	9.7	75

In each case except the first, the bulb had become iridescent, showing that non volatile boron hydrides had been formed, and a few small volatile crystals, evidently $B_{10}H_{14}$, had appeared.

Comparison of these results shows that the ratio of B_5H_{11} to diborane tends toward an upper limit, reached in a time near three months, at which point the rate of removal of the B_5H_{11}[6] becomes equal to its rate of formation. The results indicate that the preparation of B_5H_{11} at a temperature near 25° can be made most efficient by allowing each sample to stand about six weeks at a time. The B_5H_{11} so obtained is less contaminated with B_5H_9 than that obtained after longer standing at room temperature.

II. The Flow Method.—The preceding method is too slow for the preparation of large quantities of B_5H_{11}. The rate of reaction is increased greatly by exposing the diborane to higher temperatures, which must be applied only for short periods of time in order to avoid decomposing the product. The reaction is carried out quickly and conveniently by the use of a flow method, employing the apparatus shown in Fig. 1.

In this apparatus M is a 15-cc. measuring tube having 10 mm. internal diameter and 1 mm. wall thickness. The U-tube U4A is made of tubing having 15 mm. internal diameter and is 15 mm. high; its volume is 55 cc.[7] C is a small in-sealed capillary tube which regulates the flow rate. The rate of flow may be changed by replacing one capillary tube by another. The size of U4 is not critical, but it should be wide enough to allow condensation of the whole sample of diborane (one or two liters of gas) without stoppage. The system is connected through the mercury float-valve V 11 to the central tube of the apparatus.

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[5] (5) Stock, *Ber.*, **51**, 985 (1918).

[6] (6) This removal may occur by decomposition to form non-volatile solids, or by reaction with hydrogen to give diborane and tetraborane.

[7] (7) It should be mentioned that the U-tube used in our experiments happened to be etched in places (about one-fifth of the heated area). It is shown below that the formation of B_5H_{11} seems to be a wall-catalyzed reaction. The etching therefore may be a factor in determining the yield.

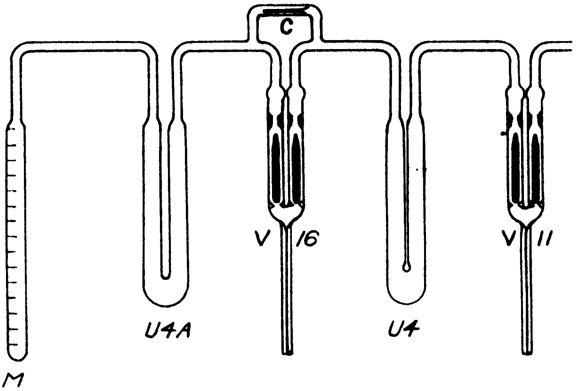

Fig. 1.

The diborane evaporates from M, which is held at a temperature of −78.5° (pressure near two atmospheres). It passes through U4A, which is kept at a suitable temperature (100 to 120°, depending on the experiment), and then goes with the reaction products through the capillary tube and is condensed in U4 at −196°. The hydrogen, which passes into the central tube, is pumped out by a Töpler pump and measured. Its quantity serves as an indication of the extent of reaction. The condensate in U4 may be returned to M and the process repeated again and again, to convert any desired fraction of the diborane into B_5H_{11} and B_4H_{10}. The results of these experiments are shown in Table II.

TABLE II

Conditions			Products, cc. of gas			Results		
Effective vol. of diborane, cc.	Flow rate, cc./min.	Temp. of U4A, °C.	H_2	B_4H_{10}	B_5H_{11}	B_2H_6 used up	% Reaction	Yield of B_5H_{11} + B_4H_{10}, %
1700	14	100	30.6	4.0	13.0	41	2.3	99
4620	14	100	84.0	10.4	36.2	114	2.5	99.5
6760	28	100	39.6	..	..	...	0.8	..
6640	28	110	111.0	..	..	...	2.1	..
11410	30	115	301.3	16.0	135.0	390	3.5	94.7

In this table the effective volume of diborane is the product of the average volume of the sample by the number of repetitions of the passage. The flow rate is the volume of gas (referred to standard conditions) passing through per minute. For the third and fourth of these experiments the percentage reaction was calculated by comparison with the quantities of hydrogen produced in the first two experiments. In the fourth experiment the temperature of U4A during the first five minutes was 120°. In that time 8 cc. of hydrogen was produced, and solid products appeared in the hot region. In the fifth experiment the temperature sometimes rose as high as 119° for short periods of time. It is believed that the main loss of material, due to the formation of solids, occurred during such intervals. There is good reason to believe that 115° is the temperature for greatest efficiency under the conditions here described.

Physical Constants.—The most trustworthy determinations of the vapor tensions and melting point of B_5H_{11} were made with a sample obtained from 1100 cc. of diborane which had stood six weeks in diffuse light at room temperature, in the presence of 300 cc. of hydrogen. The sample, 5.6 cc. of gas, was subjected to a long series of fractional condensations, by which 4.6 cc. of it was purified to the last possible degree. The vapor tensions of all fractions of this sample were exactly the same: 53.0 mm. at 0° (mercury at room temperature). The two determinations of the melting point of this sample gave the values −123.3° and −123.4° (measured by means of the ethylene vapor tension thermometer).

The vapor tensions were measured at different temperatures, established in a well-stirred ether bath and measured by means of a carefully calibrated alcohol thermometer (graduated to 0.2°). Each value given in Table III is the average of at least two measurements. The pressures were corrected to 0° by subtracting 0.45%.

TABLE III

t, °C.	−43.6	−39.0	−35.8	−33.4	−31.5	−25.5	−23.4	−20.2
p, mm.	3.5	5.0	6.1	7.2	8.5	12.2	14.0	17.0
t, °C.	−16.4	−13.4	−9.6	−7.0	−2.8	0.0	8.4	
p, mm.	21.7	25.6	32.1	35.8	45.6	52.8	77.7	

These values deviate less than 0.5° from the equation

$$\log_{10} p = 7.901 - (1690.3/T)$$

From this we calculate that the molal heat of vaporization is 7734 cal., and the normal boiling point, 63°. The Trouton constant is found to be 23.0 cal./deg. This abnormally high value suggests that any values taken at higher temperatures would have fallen below those predicted by the linear equation given above. The true boiling point might be one or two degrees higher than that given.

Results obtained with another sample illustrate the importance of selecting a sample as free as possible from B_5H_9. A 65-cc. sample (combined products of the second and third experiments of Table I and the first and second of Table II) was divided into eleven fractions; the middle seven showed vapor tensions varying 0.5 mm. from the average 54.5 mm., and melting points varying as much as 0.4° from the average value −123.2° A 7.48-cc. portion of the sample, decomposed completely in a heated quartz tube, gave 5.49 volumes of hydrogen and a weight of boron corresponding to 4.86 volumes of gas. It is evident that such an analysis is not sensitive enough to detect the small quantity of B_5H_9 which seems to have been present.

The vapor tension values reported by Stock and Pohland[8] agree well with our values at low temperatures, but deviate markedly at higher temperatures (4 mm. high at 0°). It is evident that their sample was free from tetraborane, but must have been considerably contaminated with B_5H_9. This is to be expected in a sample accumulated in a period of ten months. One of our samples, obtained from diborane which had stood for thirteen and one-half months at room temperature, was analyzed by complete thermal decomposition and found to contain about 12% B_5H_9. Its vapor tension at 0°, after the most rigorous fractionation, was 57 mm. The melting point was three degrees lower than that of our purest sample. The presence of B_5H_9 in carefully purified pentaborane samples is indicated very well by the deviation of the vapor pressure at 0° from the value 53.0 mm.

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[8] Stock and Pohland, *Ber.*, **59B**, 2211 (1926).

Heavier By-product of the Preparation.—The tenth fraction of the 65-cc. sample, 1.65 cc., had a vapor tension of 53 mm. at 0°, and the residue, 0.57 cc., only 23 mm. The latter was subjected to further fractionation, until a sample (0.25 cc.) having 10-mm. vapor pressure at 0° was obtained. The quantity was too small for positive identification, even by the very fine scale methods now available. Its volatility indicated a hexaborane; whether impure B_6H_{10} or an undiscovered hexaborane cannot be decided until a larger sample is available.

The Thermal Decomposition of B_5H_{11}

Preliminary Experiments.—A number of experiments, for the purpose of obtaining a qualitative idea of the behavior of B_5H_{11}, were performed. In most of these experiments the temperature was 100° and the container had a volume five or six times as great as the standard volume of the sample. It was learned that B_5H_{11} decomposes to give hydrogen, diborane, tetraborane, B_5H_9, $B_{10}H_{14}$ and a non-volatile yellow solid (evidently a mixture), easily hydrolyzable, but insoluble in any ordinary solvent. The yields of tetraborane and diborane were highest when the period of heating was short (ten minutes or less at 100°). The yields of B_5H_9 and $B_{10}H_{14}$ increased with the duration of heating. In most cases only unweighable traces of $B_{10}H_{14}$ were obtained. It was found, however, that reasonable yields of this substance were produced if one end of the tube remained at room temperature while the other end was heated. Neither B_5H_9 nor $B_{10}H_{14}$ appeared in detectable quantity before many other substances had been formed; in one experiment, for example, the sample was heated for twelve minutes at 100°, and was 75% decomposed to produce diborane, tetraborane and non-volatile solids. Only the minutest trace of $B_{10}H_{14}$ was produced, and the B_5H_9 was not detectable.

The non-volatile solid appeared only on the lower side of the container; it seemed to be formed by a homogeneous reaction, and then precipitated as a fine, gummy powder. Moreover, the formation of this substance could not be observed at all after the first hour at 100°, as shown by inverting the container at that time. This observation was explained by further experiments which showed that hydrogen inhibits the formation of the brown solids to a marked degree.

The Incipient Decomposition of B_5H_{11}.—It was observed in the preliminary experiments that a red-brown ring, appearing like the result of condensing a liquid which solidified afterward, always formed on the cool part of any of the tubes not completely immersed in the heating bath. This result made it seem worth while to search for a compound intermediate between B_5H_{11} and the brown solid which seemed to be one of its final decomposition products. In the first experiment in this direction, a 50.7-cc. sample of B_5H_{11} stood for seven and one-half hours at 25° (mainly in the liquid state), and 10% of it was decomposed to produce hydrogen, diborane, tetraborane, a trace of the brown solid, and a quantity of slightly volatile material too small for further study. In another experiment, 80.0 cc. of B_5H_{11} was held at 0° for eighty-eight hours, under conditions such that the reaction products more volatile than B_5H_{11} were removed as soon as they were formed. Five per cent. was decomposed, but the quantity of slightly volatile material again was too small to allow definite conclusions to be drawn.

Since these simple methods led to no clear-cut results, evidently because of the instability of the desired substance, we tried next a flow method. A 75-cc. sample of B$_5$H$_{11}$ was placed in M (Fig. 1) and allowed to pass through U4A at 50°, under the pressure of its vapor at 22°. The rate of flow was such that the sample evaporated in thirty minutes. The flow was stopped twenty minutes later, and 0.2 cc. of hydrogen was pumped off. The products more volatile than B$_5$H$_{11}$ (diborane and tetraborane) amounted to 0.4 cc. The remaining pentaborane was distilled very slowly through a U-tube immersed in a bath at $-60°$, and the fraction condensed at that temperature was found to consist of a very small quantity (estimated 0.1 to 0.2 cc. gas at standard conditions) of a substance having a vapor tension near 1 mm. at room temperature.

This process was repeated four times, with U4A at 65° (same sample of pentaborane); in each case the process was stopped as soon as the evaporation was complete. The reaction products were 2.5 cc. hydrogen, 3.75 cc. diborane, 1.00 cc. of tetraborane, and 0.5 cc. (gas) of a substance whose vapor tension at 24° was 1.2 mm. A small quantity of the brown non-volatile solid appeared in U4A. The slightly volatile substance was purified by the method of fractional condensation (trapped at $-33°$). Its uniformity was established by the fact that the vapor tension remained exactly the same while the volume of the apparatus was doubled and then tripled; about three quarters of the sample then was in the gas phase. The substance was found to be decidedly unstable: the vapor tension of a 0.15-cc. sample increased from 1.2 mm. to 1.7 mm. in five minutes at room temperature.

Evidence of the Existence of an Octaborane.—The most direct evidence for the belief that this substance is an octaborane is derived from the value of its vapor tension at 24°. The temperature at which each of the known hydrides of boron has a vapor tension of 1.2 mm. may be calculated from the vapor tension–temperature curves, and found to be as follows: B$_2$H$_6$, $-162°$; B$_4$H$_{10}$, $-90°$; B$_5$H$_{11}$, $-58°$;[9] B$_6$H$_{10}$, $-28°$;[10] B$_{10}$H$_{14}$, 63°. If we plot the temperature against the number of boron atoms in the molecule, we obtain a very regular curve whose intercept at 24° corresponds to 8.05 ± 0.10 boron atoms. It seems reasonably safe to conclude that the slightly volatile substance was an octaborane.

The Behavior of B$_5$H$_{11}$ and B$_4$H$_{10}$ with Hydrogen.—The details of the experiments on the behavior of B$_5$H$_{11}$ with hydrogen are given in Table IV. In each experiment the sample was condensed in the bottom of the container (in most cases a bulb of the shape represented in Fig. 2); then pure hydrogen was added until the pressure was 750 mm., and the container was sealed off. On account of the low temperature of the lower end of the tube, the volume of the hydrogen (standard conditions) in most cases was 15–25% higher than the recorded volume of the bulb (fourth column). After immersion for a sharply controlled time in water at 100°, each bulb was cooled rapidly to room temperature and the contents at once introduced into the vacuum apparatus by means of the tube opener. In pumping the hydrogen out through a trap immersed in liquid nitrogen, it was not always possible to avoid some small loss of diborane. Each mixture of reaction products was separated completely into its components by the method of fractional condensation, and the volume of each component determined. The quantity of B$_5$H$_9$ in each of the pentaborane

(9) Data for B$_5$H$_9$ below the melting point are not available.

(10) Estimated from the vapor tension at 0° (compared with B$_5$H$_{11}$ by the use of Dühring's rule).

residues from experiments 2, 3 and 4 was determined by decomposing the measured sample in a hot quartz tube and measuring the volume of the hydrogen produced. These determinations were based on the reasonable assumption that the residues contained only B_5H_9 and B_5H_{11}.

In most of these experiments there was no observable formation of solids. Experiment 7 is exceptional, in that there was no hydrogen present at the start—brown solids therefore were formed. In each of Experiments 3c, 4b, and 4c, a barely observable scum of white non-volatile solid appeared.

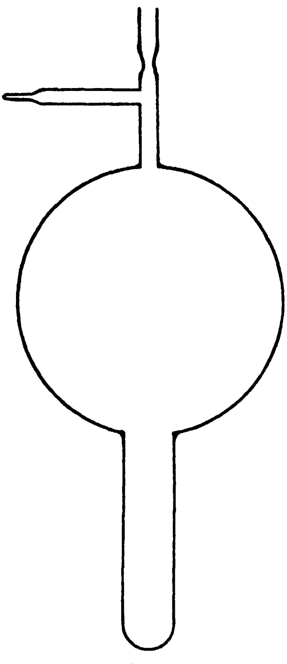

Fig. 2.

Attention is called to the fact that the term "pentaborane" used in the headings of several columns in Table IV refers to mixtures of B_5H_9 and B_5H_{11}. As has already been pointed out, it is exceedingly difficult to prepare samples of the latter entirely free from the former. For our present purpose a slight contamination is of no significance, provided due allowance is made for it in interpreting the results. Present analytical methods do not permit a determination of the amount of B_5H_9 in a sample of nearly pure B_5H_{11}. The data of column 10, "Percentage of pentaborane used up" therefore cannot be accurately transformed into "Percentage of B_5H_{11} used up" because we do not know precisely how pure the original samples in each experiment were. But we can show by the following analysis of the data that the error thus introduced cannot be large.

In Expts. 2 and 3, different portions of the same sample of "pentaborane" were heated at 100° for different periods. The product was then fractionated and the residual "pentaborane" was in each case reheated (2b, 3b). In Expt. 3 this procedure was repeated once more. Experiment 4 was similar, except that a different sample of "pentaborane" was used. As a result of the heating process, the percentage of B_5H_{11} in the residue was decreased to such an extent that a fairly reliable analysis of the percentage of B_5H_9 could be made. If we assume as a first approximation that none of the B_5H_9 thus found was a product of the reaction, *i. e.*, that all of it was present in the original samples, we should conclude that sample 2 originally contained 6.3%, sample 3, 5.3%, and sample 4, 3.2% B_5H_9. But these represent maximum values,[11] even though they represent relatively small contamination with B_5H_9. The difference in the percentage of B_5H_9 found for samples 2 and 3, on the assump-

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(11) It has been shown by separate experiments that the treatment to which these samples was subjected does not appreciably affect B_5H_9. Of a sample of fairly pure B_5H_9, heated for five days at 125°, only 2% had undergone change.

TABLE IV

Conditions					Results						
1	2	3	4	5	6	7	8	9	10	11	12
Expt.	Vol. of pentaborane, cc.	Tension of pentaborane, at 0°, mm.	Vol. of container, cc.	Time of heating, min.	Vol. of residual pentaborane, cc.	Vol. of B_2H_6, cc.	Vol. of B_4H_{10}, cc.	Vol. of pentaborane used up, cc.	% Pentaborane used up	Tension pentaborane residue at 0° mm.	Final vol. of B_4H_9, cc.
1[a]	5.30	54.5	30 ·	5	0.85	5.75	2.40	4.45	84	..	..
2a	22.2	54.4	370	10	5.90	10.7	14.8	16.3	74	56	..
2b	5.90	56	123	6	2.86	1.72	2.86	3.04	52	58	1.4
3a	42.2	54.5	565	4	24.5	9.05	17.0	17.7	58	55	..
3b	24.5	55	370	8	8.0	9.1	15.0	16.5	67	58	..
3c	8.00	58	123	20	2.66	6.2	2.64	5.34	67	63.5	2.25
4a	31.6	53.5	370	8	10.7	...	..	20.9	66	54.5	..
4b	10.7	55.0	123	20	2.80	...	..	7.90	74	56	..
4c[a]	2.80	56	30	25	1.85	...	..	0.95	34	61	1.0
5[b]	28.8	54.5	370	10	15.10	12.0	1.37	13.7	47	..	..
6	28.6	54.5	370	10	7.40	13.3	19.7	21.2	74	..	..
7[c]	27.5	54.5	358	10	6.90	15.2	18.0	20.6	75	..	..
8[d]	37.2	54.5	370	78 hrs.	35.35	1.60	1.50	1.85	5	..	..

[a] The container for this experiment was a cylindrical tube. Quantity of hydrogen, 60 cc. [b] No hydrogen present at the start. 8.35 cc. produced during the course of the experiment. [c] The container for this experiment was a series of bulbs, having an estimated ratio of wall area to volume 80% greater than that of the single large bulb used in experiment 6. [d] Entirely at room temperature.

tion that it was all present in the original sample, is too large to be explained by experimental error alone. It must, therefore, be due to the *formation* of more B_5H_9 during the reaction in Expt. 2 than during Expt. 3. This is just what would be expected, for in Expt. 2 the main portion of the material was heated a longer time than in Expt. 3. If this is true, then some of the B_5H_9 found in Expt. 4 must also have been a reaction product.

Hence we conclude that the samples used in Expts. 2 and 3 must have contained considerably less than 5% of B_5H_9 while the sample used in Expt. 4 must have contained less than 3% of B_5H_9. Not only are the total amounts of B_5H_9 relatively small in these samples, but the difference between the amount of contamination is small. Nevertheless, the sample used in Expts. 2 and 3 showed a vapor tension of 54.5 mm. at 0°, while the sample used in Expt. 4 showed 53.5 mm. The vapor tension at 0° thus is shown to be a very sensitive test of the degree of contamination. In the following, we shall consequently assume that two samples showing the same vapor tension, provided its value is not far from 53 mm., have the same composition.

Comparison of Expts. 2a, 3a, 4b, 6 and 7, all of which employed samples of pentaborane[12] having approximately the same vapor tension at 0°, shows that the initial reaction is fairly rapid, but that it soon becomes very slow. In four minutes (Expt. 3a), 58% of the pentaborane had been decomposed and in ten minutes about 75% (Expts. 2a, 6 and 7). Further heating, however, causes but little further change, for the percentage was

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(12) Experiments 1 and 5 are not included here because the conditions under which these were carried out were different from those of the others.

only slightly higher after twenty minutes of heating (Expt. 4b, in which the percentage reaction is slightly higher than the indicated 74%, because of higher B_5H_9 content). In Expt. 3a the amount of tetraborane formed differs by only 4% from the amount of B_5H_{11} used up, and the amount of diborane produced is slightly over one-half this quantity. These proportions agree reasonably well with the equation $2B_5H_{11} + 2H_2 \leftrightarrows 2B_4H_{10} + B_2H_6$. The deficiency of tetraborane and the excess of diborane are satisfactorily explained by a slower secondary reaction of the tetraborane to form diborane. In the other experiments under discussion, the discrepancies are larger, but always in the same direction; this is due to the fact that in these the time of heating is longer and the secondary reaction, therefore, has had time to proceed farther.

The situation was made clear by experiments in which tetraborane was heated with hydrogen. The tetraborane used for these experiments was obtained in very pure condition (vapor tension 388 mm. at 0°) by fractionating the products of the reaction of B_5H_{11} with hydrogen. The experiments, which are numbered as a continuation of Table IV, were as follows.

9. The bulb used in experiment 6 was filled with 14.1 cc. of tetraborane and somewhat more than one atmosphere pressure of pure hydrogen. During twenty minutes at 100°, 6.05 cc., or 43%, of the tetraborane was converted into 10.65 cc. of diborane and 0.45 cc. of B_5H_{11} (nearly pure).

10. The six-bulb container used in Expt. 7 was filled with 13.9 cc. of tetraborane and the usual excess of hydrogen. During twenty minutes at 100°, 7.40 cc., or 53%, of the tetraborane was converted into 12.30 cc. of diborane and 0.75 cc. of B_5H_{11} (vapor tension 54 mm. at 0°).

These results show that tetraborane reacts with hydrogen to form diborane, at a rate accounting very well for the deviations from the equation $2B_5H_{11} + 2H_2 \rightleftarrows 2B_4H_{10} + B_2H_6$. They also show that this reaction is reversible, a fact which may throw light on the sudden slowing of the reaction. But this reverse reaction is only a part of the reaction of tetraborane; it appears that most of it is converted into diborane. The final result must be an equilibrium[13] in which diborane is the predominating boron hydride. This statement is confirmed by the results of an experiment in which diborane and hydrogen were heated together for sixty-four hours at 100°. At the end of this time the 250-cc. bulb contained 150 cc. of hydrogen, 38 cc. of diborane, 0.5 cc. of B_4H_{10} and 2.2 cc. of pentaborane (nearly pure B_5H_9), along with some white solids.

The difference in the percentage reaction of tetraborane in Expts. 9 and 10 shows that the rate of reaction of tetraborane with hydrogen depends upon at least one wall-catalyzed process. It is especially evident that the rate of formation of B_5H_{11} is increased by increasing the wall area, for the concentration of this substance at the end of each experiment was greater in number 10, which was carried out in a vessel of larger wall area.

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[13] Even this equilibrium is slowly shifted by the irreversible formation of B_5H_9, $B_{10}H_{14}$ and nonvolatile solids. We may treat it as a true equilibrium because it can be established before any important quantities of these other substances are formed.

Comparison of the behavior of B_5H_{11} with and without initial hydrogen at 100° (Expts. 5 and 6) shows that considerably more reaction occurs when hydrogen is present than when it is absent. This result is plausibly explained by supposing that the B_5H_{11} molecule first breaks up into radicals, which recombine to a large extent when hydrogen is absent. But a large excess of hydrogen prevents much of this recombination because these active radicals unite with it to form diborane and tetraborane, substances whose enduring qualities are greater than of B_5H_{11}; the reforming of B_5H_{11} is thus delayed. The alternate explanation, that hydrogen itself attacks the pentaborane chain, does not seem very probable.

In Expt. 8, which occurred at room temperature, it seems that the reaction of tetraborane with hydrogen occurred at a rate proportionally higher than in similar experiments at 100°; only 5% of the pentaborane was used up, yet the deficiency of tetraborane, below that required by the equation $2B_5H_{11} + 2H_2 = 2B_4H_{10} + B_2H_6$, was 19%. There might be many ways to account for this difference, but no uniquely satisfactory explanation appears.

The Preparation of B_5H_9.—We have performed a number of experiments in the direction of finding the most favorable conditions for the reaction by which diborane is converted into B_5H_9.[14] At the present writing the highest yield obtained represented only 33% of the volatile boron hydrides used up. It was found that a high concentration of hydrogen is an advantage, for it seems to interfere not at all with the rate of formation of B_5H_9, but hinders greatly the formation of non-volatile solids. Hydrogen chloride is not essential to the reaction, but it increases the yield. For this purpose, however, boron trichloride is quite as useful, and has the advantage that it does not convert boron hydride to boron chloride. The temperature used in most of the experiments was 120–130°; at 100° the yields were only about half as high, under comparable conditions. It was found most efficient to heat for three days at a time. The highest yield resulted when the diborane contained a fair quantity of tetraborane at the start; yet the use of a high concentration of tetraborane did not improve the yield, doubtless because of its comparatively rapid conversion to diborane under these conditions. Similar results were obtained when B_5H_{11} was heated for several days at 120°, with approximately one-third of its volume of boron trichloride and a large excess of hydrogen.

Much work is still to be done before we can be certain of the best conditions for the preparation of B_5H_9. This work is hindered by the lack of adequate working hypotheses concerning the mechanism of the reaction and the function of the boron chloride.

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(14) Schlesinger and Burg, THIS JOURNAL, 53, 4331 (1931).

Summary

The preparation of B_5H_{11} in quantities suitable for experimental work has been accomplished by the use of a flow method involving diborane. Measurements upon a sample unusually free from B_5H_9 gave $-123.3°$ for the melting point and 53.0 mm. for the vapor tension at 0°.

The thermal decomposition of B_5H_{11} at first gives hydrogen, diborane, tetraborane and smaller quantities of a probable octaborane. Further heating produces non-volatile solids, B_5H_9 and $B_{10}H_{14}$. A ten-fold excess of hydrogen added at the start hinders so effectively the formation of substances less volatile than B_5H_{11} that it is possible to prepare diborane and tetraborane from B_5H_{11} practically without loss. The equilibrium system involving hydrogen, B_5H_{11}, tetraborane and diborane was studied to some extent at a temperature of 100°. Any one of these three boron hydrides may be prepared in quantity from one of the others, by a suitable adjustment of the experimental conditions. The preparation of useful quantities of tetraborane from diborane therefore is feasible.

Improvements in the method of preparing B_5H_9 by long heating of diborane have increased the yields to 33%.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. III. Dimethoxyborine

BY ANTON B. BURG AND H. I. SCHLESINGER

Linkages between boron atoms seldom occur in compounds of boron with elements other than hydrogen. A striking contrast to this situation is presented by the boron hydrides, in all of which the boron atoms are linked together. The tendency for such linking is so strong that monoborine (BH_3) seems incapable of existence and the simplest hydride is diborane (B_2H_6), a circumstance not easily explained by any generally acceptable theory of valence. Substitution of halogens for hydrogen in diborane leads to compounds of the type B_2H_5X[1] and possibly $B_2H_4X_2$, but further substitution leads only to the boron trihalide. The only known simple derivative of monoborine, aside from those in which all of the hydrogen is replaced, is phenylborine ($C_6H_5BH_2$),[2] a compound which has been studied very little. It is thus of considerable interest to prepare compounds of the types HBR_2, H_2BR, HBX_2, and H_2BX, in the hope that a compound showing a tendency toward association by boron linkages may be obtained. Such work might lead to a better understanding of the factors which stabilize the boron to boron bond.

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(1) Stock, Kusz and Priesz, *Ber.*, **47**, 3115 (1914); Stock and Pohland, *ibid.*, **59B**, 2223 (1926).

(2) Pace, *Atti. accad. Lincei*, [VI] **10**, 195 (1929).

This paper describes the preparation of dimethoxyborine, $(CH_3O)_2BH$, by the reaction of diborane with methyl alcohol. It is a colorless liquid, whose normal boiling point is 25.9° (vapor tension 275 mm. at 0°). In the vapor phase at room temperature it shows a normal value of the molecular weight (73.9), and the only indications of association at lower temperatures are too uncertain to be considered. It is not spontaneously inflammable in air, but is rapidly hydrolyzed according to the equation $(CH_3O)_2BH + 3HOH \longrightarrow B(OH)_3 + 2CH_3OH + H_2$. Its odor is a composite of methyl alcohol and diborane.

Dimethoxyborine decomposes reversibly, according to the equation $6(CH_3O)_2BH \rightleftarrows B_2H_6 + 4(CH_3O)_3B$. No intermediate compound, such as monomethoxyborine or methoxydiborane, could be isolated. The equilibrium point favors the decomposition under all easily attained conditions. The rate of decomposition in the gas phase is comparatively low, and depends but little upon changes of pressure. In the liquid state at temperatures above 0°, the decomposition is so rapid that special precautions are necessary for obtaining trustworthy measurements of the vapor tension.

In all of this work, the only indication of the existence of monomethoxyborine was an unstable, non-volatile white solid, which was formed as a by-product of the preparation of dimethoxyborine. It decomposed on standing at room temperature, to give diborane, dimethoxyborine, and trimethyl borate, in proportions represented by the formula $(CH_3OBH_2)_x$. The substance may have been a polymer of monomethoxyborine, which could be explained as a complex compound in which oxygen in one molecule occupies the fourth position in the coördination sphere of the boron in another. This is not certain, for other explanations are possible.

Experimental

Preparation.—The reaction used for the preparation is represented by the equation $4CH_3OH + B_2H_6 \longrightarrow 2(CH_3O)_2BH + 4H_2$. The methyl alcohol used for the purpose was treated with barium oxide to remove water, and its purity was checked by the vapor tension at 0° (29.6 mm.). The exact proportions of the two substances apparently were not critical, for the yields were about equally good whether the excess of diborane was four-fold or twenty-fold. The yields varied between 75 and 90% of the methyl alcohol; trimethyl borate was obtained as a by-product. The details of our largest-scale preparation were as follows.

Approximately 500 cc.[3] of pure diborane and 270 cc. of methyl alcohol were condensed together upon the outer wall of a 3-cm. wide test-tube, which was sealed into the top of a one-liter flask[4] connected to the vacuum apparatus. Then the two substances were allowed to warm and a rapid effervescence occurred. The hydrogen was pumped off through a trap immersed in liquid nitrogen, and the process was repeated until no further hydrogen was produced. Then the excess diborane was isolated by trapping

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(3) All volumes given in this paper refer to gases at standard conditions.

(4) This reaction vessel is like that used by Stock and Somieski, *Ber.*, **50**, 1742 (1917), for the halogenation of silane.

out the less volatile substances at a temperature of −145°, and two more 270-cc. portions of methyl alcohol were treated with it as before. The dimethoxyborine was purified by fractional condensation, using baths at −90° (to trap out methyl borate completely) and −120°. The fraction condensed at −120° showed a vapor tension of 275 mm. at 0°; further distillation did not change the value; yield, 300 cc.

Analysis.—A sample was analyzed by hydrolysis with a slight excess of water, according to the equation $(CH_3O)_2BH + 3HOH \longrightarrow B(OH)_3 + 2CH_3OH + H_2$. The hydrogen was pumped out and measured. The methyl alcohol was separated from the residual water by distillation methods, and measured as a gas. The boric acid was titrated with 0.1 *N* barium hydroxide, in the presence of excess mannite. A sample whose volume was 8.85 cc. gave 8.95 cc. of hydrogen, 17.5 cc. of methyl alcohol, and 8.85 cc. of boric acid (calculated as a gas). These values check the above equation, leaving no doubt of the identity of the substance.

Solid By-Product of the Preparation.—An unstable white solid was formed as a by-product of the experiment described above. It seemed to be entirely non-volatile at room temperature, but decomposed on heating. The volatile substances were removed completely from the reaction vessel, and the solid was allowed to stand for twelve hours at room temperature. During this time it disappeared completely, and in its place was found 16.0 cc. of diborane, 18.0 cc. of dimethoxyborine, and 6.6 cc. of trimethyl borate. These quantities correspond to the formula $(CH_3OBH_2)_x$, within the probable error.

At first glance this substance appears to be a polymer of monomethoxyborine, which is easily explained as a complex compound in which oxygen in one molecule occupies the fourth position in the coördination sphere of boron in another. But we might also regard it as a complex compound of the type $(CH_3OBH_3)_2BOCH_3$, or $(CH_3OBH_3)BH(OCH_3)$. These possibilities are less probable, in that they require that the hypothetical BH_3 form complex compounds with oxygen, but the present state of our knowledge does not allow us to eliminate them.

The molecular weight was determined by weighing a measured volume of the gas, in a small bulb closed by a stopcock (the substance reacts slightly with grease, but the effect is not serious): first sample, 18.32 cc. weighed 0.0604 g., m. w. = 73.8; second sample, 37.90 cc. weighed 0.1256 g., m. w. = 74.2. The theoretical value for the monomer is 73.9.

The melting point was determined by the aid of the magnetic device of Stock.[5] The temperature was measured by the carbon tetrafluoride vapor tension thermometer. The average value was −130.6°.[6]

The vapor tensions were measured with particular care, on account of their possible relation to association in the liquid state at low temperatures. A 200-cc. sample was purified as thoroughly as possible by the aid of a simple reflux fractionating tube[7] (reflux temperature, −78.5°) and stored at liquid air temperature. Almost all of the measurements were made upon fresh small samples from this large supply. The tensions at temperatures below −40° were registered upon a mercury manometer whose arms were 16 mm. in internal diameter, and measured by a precision cathetometer (probable error not greater than 0.01 mm.). At higher temperatures it was necessary to work more rapidly than the use of the cathetometer would allow. The values given in Table I are either averages of several points near together, or selections from a number of mutually consistent values.

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(5) Stock, *Ber.*, 50, 156 (1917).

(6) It was noted that slightly different values were obtained, depending upon whether the same sample was melted on the plunger and re-frozen before the determination, or condensed directly as a solid, during a very slow distillation. In the former case, the average was −130.2°; in the latter, −131.0°. The difference is greater than the probable error, but its meaning is not apparent.

(7) Burg, article to be published in an early number of THIS JOURNAL.

TABLE I

t, °C.........	−95.8	−86.7	−70.9	−64.7	−56.1	−46.3	−36.0	−28.2
p, mm........	0.18	0.52*	2.66	4.58	9.60	19.85*	39.2	64.3
t, °C.........	−20.5	−11.5	−8.9	0.00	6.8	8.9	12.0	13.8
p, mm........	100.5	158	180	275*	366	403	453	490

The values marked with an asterisk were used in calculating the constants for the equation

$$\log_{10} p = -(1849.0/T) + 175 \log_{10} T - 0.008221\, T + 7.1895$$

which represents the other values reasonably well. From this equation we calculate the boiling point to be 25.9°, the molal heat of vaporization, 6138 cal., and the Trouton constant, 20.5 cal./deg. The curve representing the relation of log p to $1/T$ (Fig. 1)[8] is definitely concave downward, but this curvature is not much more pronounced than that observed in many other volatile oxygen compounds. We cannot attribute it to any tendency toward formation of linkages between boron atoms.

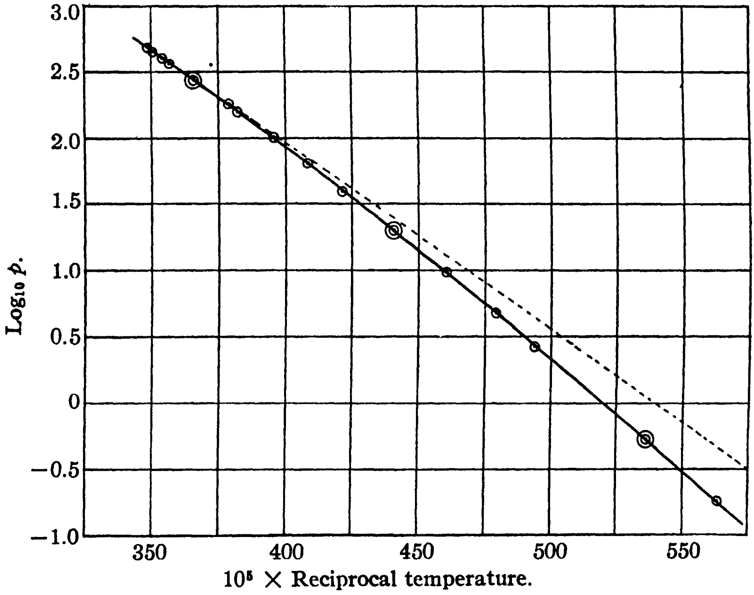

Fig. 1.—Vapor tensions of dimethoxyborine.

The Equilibrium with Diborane and Trimethyl Borate

The Decomposition.—Dimethoxyborine decomposes to form diborane and methyl borate, without indication of any other substance. The change of volume in the process, indicated by the equation $6(CH_3O)_2BH \rightleftarrows B_2H_6 + 4(CH_3O)_3B$, makes it possible to follow the change roughly by measurements of the total gas volume. Table II gives the results of an experiment in which 31.8 cc. of pure dimethoxyborine was placed in a U-tube with adjacent manometer (total available space, 105 cc.), and the volumes determined from time to time by measurement of the pressure and of the temperature, which varied one or two degrees from the average, 20°.

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[8] The dotted line represents the Clapeyron equation, drawn through the point for 0°, with a slope corresponding to a normal value for the Trouton constant. The points used for calculating the Nernst equation are doubly circled.

TABLE II

Time, hours	0	20.0	26.5	44.5	57.5	68.0
Volume, cc.	31.8	30.8	30.4	29.8	29.5	29.3

At the end of the experiment, the residual substance and the products were isolated, and it was found that 14.7 cc., or 46%, of the sample had decomposed to form 9.8 cc. of trimethyl borate[9] and 2.5 cc. of diborane, in good agreement with the equation given above and with the observed decrease of volume. The remaining 17.1 cc. of dimethoxyborine was allowed to stand for two hundred and thirty-four hours in a space of 1200 cc. at room temperature. The result was 65% decomposition. In another experiment, a 43.9-cc. sample was allowed to stand for fifteen hours in the 1200 cc. space at room temperature, and was 9% decomposed. In this case the pressure was only one-tenth as high as in the experiment recorded in Table II, but the rate of decomposition was two-thirds as rapid.

The decomposition is far more rapid if the substance is placed in the reaction vessel in which the preparation was carried out, after the disappearance of the white solid. Under such conditions a 300-cc. sample in a space of 1100 cc. was 30% decomposed in one hundred and ten minutes at room temperature. The rate was about seventeen times as rapid as that observed in the experiment recorded in Table II, which occurred at about the same pressure. The catalytic activity of the reaction chamber was destroyed by heating at high vacuum.

The Reverse Reaction.—As a test of the reversibility of the decomposition of dimethoxyborine, 17.2 cc. of diborane and 9.75 cc. of methyl borate (both very carefully purified) were placed together in a space of 105 cc., and left for forty hours in the vapor state at room temperature. The components of the mixture were separated again, and there was isolated 0.15 cc. of a gas having a vapor tension of 1.2 mm. at −78.5°. The process was repeated, this time for seventy-eight hours, and 0.30 cc. of the product was obtained. In ninety-eight hours, 0.40 cc. was produced. The three samples were combined and purified as thoroughly as possible. From two values of the vapor tension, 46 mm. at −33.8° and 17.2 mm. at −48.5°, the substance was indicated to be dimethoxyborine. All doubt was removed by an analysis, in which the 0.78-cc. sample was hydrolyzed to produce 0.8 cc. of hydrogen and 0.75 "cc." of boric acid (methyl alcohol not determined).

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[9] Identified by the 35.5 mm. vapor tension at 0°, and the value −29° for the melting point. *Cf.* Wiberg and Sütterlin, *Z. anorg. allgem. Chem.*, **202**, 15 (1931).

The decomposition of dimethoxyborine is thus shown to be appreciably reversible. This reaction is not recommended as a means of preparation, even though the yields would be practically quantitative, for any attempts to increase the rate of reaction by heating would be likely to result in some formation of B_5H_{11} and B_4H_{10}, either of which would be very hard to remove from the product.

We are planning to study further the chemical properties of dimethoxyborine, as well as the reaction of a variety of alcohols with various boron hydrides. We have recently found that boron trimethyl, like boron trihalides and trimethyl borate, reacts with diborane. We hope in the near future to be able to report on some new derivatives of diborane, obtained by this method.

Summary

Dimethoxyborine, a compound of the new type HBX_2, has been prepared by the reaction of diborane with methyl alcohol. A white, non-volatile, unstable solid which may be a complex polymer of monomethoxyborine, was obtained as a by-product.

Dimethoxyborine shows no tendency toward association, beyond that common to most volatile oxygen compounds. Its vapor tensions were measured with some care, and expressed by an equation of the Nernst approximation type.

The substance decomposes very easily to form diborane and trimethyl borate. This reaction is reversible to an appreciable extent.

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The Quantum Yields of the Photochemical Reactions of Phosgene

BY C. W. MONTGOMERY AND G. K. ROLLEFSON

In the previous work which has been reported[1] on the photochemical oxidation of phosgene, the phosgene-sensitized oxidation of carbon monoxide, and the photochemical reaction of phosgene with hydrogen, kinetic studies of the reactions have been carried out and an attempt has been made to arrive at well-correlated and self-consistent reaction mechanisms in the three cases. This program has been completely successful from the kinetic standpoint with one exception (for a discussion of this case see (1b).

Quantum Yields of the Phosgene Reaction

In order to gain further confirmation of the mechanisms already proposed, for certain photochemical reaction of phosgene it is still necessary to show that the measured values for the quantum yields of the three reactions are in agreement with the values predicted from the reaction schemes.

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[1] (a) Rollefson and Montgomery, THIS JOURNAL, 55, 142 (1933); (b) 55, 4029 (1933); (c) 55, 4036 (1933).

As a preliminary step in order to facilitate the determination of the quantum yields by eliminating one of the necessary energy measurements, it was decided first to measure the absorption coefficients of gaseous phosgene in the ultraviolet region. Although the absorption spectrum has been fully studied, no available values of the integrated over-all absorption coefficients are recorded in the literature.

For this purpose a photographic method of spectrophotometry was employed. A cylindrical quartz absorption cell 19.9 cm. long and 3.0 cm. in diameter, having plane parallel ends, was filled with phosgene to the desired pressure; the pressure was then read on the manometer, the phosgene frozen out in a convenient quartz side tube, and the absorption cell then sealed off. Photographs were taken of the absorption spectrum by means of a Hilger E-3 quartz spectrograph, using the continuum from a quartz mercury discharge tube as the source. No lenses were used as the light from the discharge tube was sufficiently intense and parallel. A fairly wide slit was used on the spectrograph in order to cut down exposure time as well as to even out any trace of band absorption which might be obtained. "Speedway" plates were used and on each plate were recorded two photographs of the absorption spectrum, two photographs of the wave length scale (which was calibrated with a quartz mercury arc), and photographs of the discharge tube with a series of calibrated screens interposed (the quartz absorption cell being kept in place but the phosgene frozen out in the side tube). The plates were then photometered by means of a Zeiss microphotometer at various intervals throughout the absorption region. Values of I/I_0 were determined by comparison of the photometer curves for the absorption region with those for the arc with screens. The absorption coefficients were then calculated according to the equation $\epsilon = (1/pl) \log_{10} (I_0/I)$, where p is the pressure of phosgene in cm. and l is the length of the cell in cm.

The results are shown in Table I. Three different plates were taken; a pressure of 10 cm. of phosgene was used for I, 5 cm. for II, and 1 cm. for III. The results are also shown graphically in Fig. 1.

Table I

Å	2745	2696	2645	2594	2543	2491	2441	2391	2342
I, $\epsilon \times 10^2$	0.15	0.26	0.41	0.63					
II, $\epsilon \times 10^2$	.13	.26	.41	.64	1.00				
III, $\epsilon \times 10^2$		.28	.50	.85	1.13	1.42	1.78	1.99	2.04

For the quantum yield measurements, a Hilger quartz monochromator D-33 equipped with a Hilger F-83 thermopile was used. The area of the monochromator slit as used was 5.08 sq. mm. The thermopile, mounted in the monochromator slit block, was calibrated against a standard lamp from the Bureau of Standards and found to have a sensitivity of 7.2 × 10^{-7} watt per mm. scale deflection with the galvanometer circuit.

The reaction vessel was similar to the cylindrical one used for the absorption coefficient determination. It was mounted flat in a cooling tank with one end about 3 mm. from a clear quartz window in the side of the tank. The transmissions of the quartz window and the plane parallel end of the reaction vessel were measured with the thermopile for the 2537 Å. line and the total transmission found to be 0.71; assuming 0.98 for the transmission of the narrow water layer between reaction vessel and window gave a total transmission for the system of about 0.70. The volume of the reaction vessel and manometer arm was measured and found to be 110 cc.

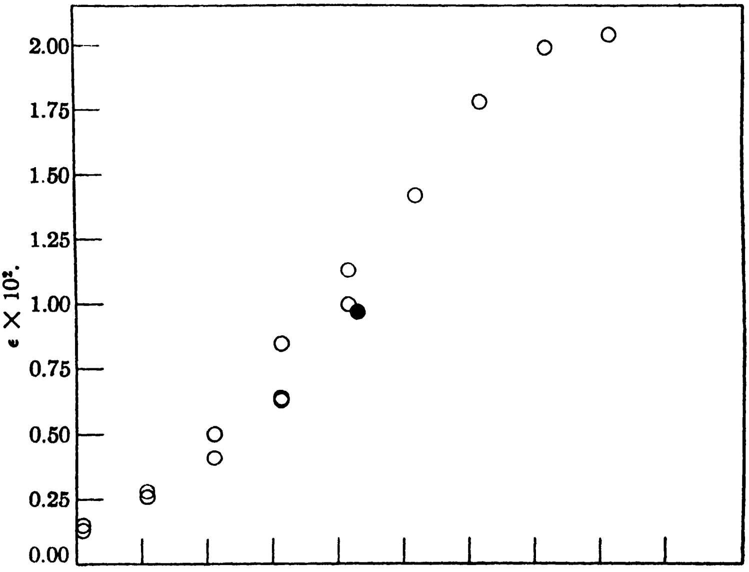

Fig. 1.

The experimental procedure was as follows. The monochromator was set on three or four prominent mercury lines visually and then turned to the 2537 region. Final setting on the line was accomplished by means of the thermopile galvanometer readings. The monochromator was then placed so that the slit was flush against the cooling tank window, directly in line with the reaction vessel. After the mercury arc had warmed up, several thermopile readings were taken. The gases were then introduced into the reaction vessel and the cooling water temperature noted. The thermopile was removed from the monochromator slit finally and illumination begun. The period of illumination varied, of course, with the reaction, sometimes being carried out for two days. At intervals during this time, thermopile readings were taken so that an average value of the rate of energy input might be obtained. Finally the manometer was read with as nearly as possible the same temperature of water in the tank as at the start (usually ±0.5°).

In order to check the value of the absorption coefficient as measured by the photographic method, a more direct measurement was made. This was done by means of the monochromator and thermopile for the 2537 Å. Hg line and gave the result $\epsilon = 0.0097$. This value is somewhat lower than the average value from Fig. 1 but is in fair agreement with the point on the curve taken from plate II. The points from plate III thus appear to be too high, and the thermopile value for ϵ has accordingly been used in the calculations. From the average rate of energy supply and the absorption coefficient of phosgene for $\lambda = 2537$ Å. ($\epsilon = 0.0097$) the amount of absorbed energy could be calculated and the number of molecules reacting was calculated, of course, from the pressure change.

I. The Photochemical Oxidation of Phosgene.—As an example of the data, the following determination is given

$P_{COCl_2} = 6.26$ cm. Hg, $P_{O_2} = 6.82$ cm. Hg
Total no. of quanta absorbed $= 4.4 \times 10^{18}$
$COCl_2$ reacting $= 16.0$ mm. $= 7.84 \times 10^{18}$ molecules
$\gamma = (7.84 \times 10^{18})/(4.4 \times 10^{18}) = 1.78$

Three similar experiments gave values for γ of 1.87, 1.73 and 1.83, the average of all four being 1.80.

II. The Phosgene-Sensitized Oxidation of Carbon Monoxide.—The quantum yield of the sensitized oxidation of carbon monoxide might be expected to vary as the ratio $(CO)^{1/2}/I_{abs.}^{1/2}$ at high pressures of oxygen and as $(CO)^{1/2}(O_2)^{1/2}/I_{abs.}^{1/2}$ at low oxygen pressures. This point was not investigated, however, as the principal object was merely to get some idea of the order of magnitude of the chain length.

Two direct measurements of the quantum yield gave $\gamma = 87$ and 95 for reaction mixtures in which the pressure of each gas ($COCl_2$, CO and O_2) was approximately 30 cm. of sulfuric acid.

An independent check on these values of γ was made by means of a comparison of the rate with the direct phosgene oxidation. Assuming 1.8 for the quantum yield of the latter reaction, γ for any other reaction in which phosgene is the absorbing substance may easily be found by comparing the rates of the two reactions, provided P_{COCl_2} and the light intensity is the same for both reactions. Several rate comparisons on the above reaction mixture were made, the rate being found to be 50–60 times as fast as the direct oxidation. This indicates a value for γ of 90–110, in good agreement with the directly measured values.

III. The Photochemical Reaction of Phosgene with Hydrogen.—No direct measurements of the quantum yield of the phosgene–hydrogen reaction were made but an idea of the value of γ can be had from a comparison of the rates of the oxidation and reduction. The following initial rate results are an example of the values obtained by comparison of rates.

$P_{COCl_2} = P_{H_2} = 40.0$ cm. H_2SO_4

t, minutes	2	4	6	8	10
γ	3.8	2.8	2.6	2.4	2.4

Discussion

In general, the results of the quantum yield determinations confirm the conclusions of the kinetic studies and the mechanisms proposed for the reactions. While the quantum yield of the oxidation is slightly lower than the value 2 predicted by the reaction mechanism, this is not a serious or unusual situation in photochemical work. Much more serious would be an experimental value greater than that predicted. There may be various factors which tend to lower the yield in this case. Although the determination of γ was made with an excess of oxygen present and the reaction was not carried out very far toward completion, still it is possible that the chlorine–oxygen ratio may be a contributing factor in lowering the rate. Furthermore, if CO_3Cl is postulated, this intermediate may take part in some side reaction which might effectively lower the rate of reaction between CO_3Cl and $COCl_2$.

The quantum yield of the phosgene-sensitized oxidation indicates that the reaction involves a long chain of the same magnitude as that of the chlorine-sensitized oxidation and further confirms the similarity of the two reactions. (For a fuller discussion of this point see (2).)

In the case of the hydrogen reaction, the relatively larger value of γ at the start of the reaction is in agreement with the proposed mechanism and rate law. As will be shown later,[1c] this higher initial rate of reaction is probably due to the second term in the rate law

$$\frac{d(CO)}{dt} = I_{abs.}\left[1 + \frac{k(H_2)}{(CO)(M)}\right]$$

which makes a large contribution to the rate at the start of the reaction, then rapidly diminishes. If it were possible to measure the quantum yield at a very short time interval after the reaction started, it is to be expected that even larger values of γ would be found. The lower limiting value of γ as shown by the first term of the above rate law should be 1.

THE PHOTOCHEMICAL REACTION OF PHOSGENE WITH HYDROGEN

Bredig and von Goldberger[2] investigated the photochemical reaction of phosgene with hydrogen. They made no attempt to study the kinetics of the reaction but were concerned solely with the stoichiometry and the question of the existence or non-existence of formaldehyde as one of the reaction products. They found that the predominant reaction (they followed it to 95–98% completion in some cases) could be represented by the equation $COCl_2 + H_2 \longrightarrow CO + 2HCl$, and, further, that formaldehyde was present "only in traces at 10°," and at 80° was not detectable. They concluded that if formaldehyde were formed in some primary process, it was probably immediately decomposed photochemically.

A study of the reaction kinetics has been made in order to determine whether a reaction mechanism could be formulated in essential agreement with those of other phosgene reactions. In the event that formaldehyde appeared to be one of the products it was thought likely that such a study might yield an insight into some new partial reactions involving the intermediate (COCl).

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(2) Bredig and v. Goldberger, *Z. physik. Chem.*, **110**, 521 (1924).

Experimental

The apparatus used was the same as that previously described for the other phosgene reactions.[1a] Phosgene was purified in the same manner as before. Hydrogen was prepared electrolytically, purified by passing over hot copper, and dried in a storage bulb containing magnesium perchlorate. Carbon monoxide was prepared and purified as before and the carbon dioxide used in the inert gas experiments was taken, without purification, from a cylinder and dried by passing through magnesium perchlorate.

In order to test the stoichiometry of the reaction, several preliminary experiments were made in which from time to time during the course of the reaction the reaction vessel was immersed in liquid oxygen and the manometer readings taken with the condensable gases ($COCl_2$ and HCl) frozen out. It was found that these liquid oxygen pressure readings remained constant throughout each experiment. It was concluded, therefore, that the above equation holds for the over-all phosgene reduction since it indicates that there should be no pressure change at liquid oxygen temperature. If formaldehyde were formed during the reaction, it might be expected that the liquid oxygen pressure readings would gradually decrease as the reaction proceeded. The constancy of the low temperature pressure readings must therefore be interpreted as substantiation of the conclusions of Bredig and von Goldberger that little if any formaldehyde is formed and that their equation holds for the over-all reaction. Furthermore, on the basis of the volume change in their equation, the reaction proceeded quite smoothly and in some experiments was carried out to 90–95% completion.

Results

The experimental results fall into two classes: those results which led to the elucidation of the initial rate law, and the results of further experiments designed to indicate how this initial law might be modified in order to be applicable over the entire course of the reaction.

The effect on the initial rate of varying the hydrogen pressure is shown by the results in Table II.

Table II

H_2, cm. H_2SO_4	4.93	15.07	25.20	50.00
Rate, cm. H_2SO_4/min	0.560	0.573	0.600	0.617

Although the hydrogen pressure was varied ten-fold, there is but little change in the initial rate. There is unquestionably a trend, however, toward higher initial rate as the hydrogen pressure increases, but the rate, at most, appears rather insensitive to variations in the hydrogen pressure.

Table III shows the results of a series of experiments in which the effect of varying the phosgene pressure was investigated. Pressures are expressed in cm. and initial rates in cm./min.

From the rates and the phosgene pressures alone, it is impossible to decide how ($COCl_2$) enters the rate law. The rate has an upward trend but appears to approach a limiting value at high phosgene pressures. This apparent independence of the rate on the phosgene pressure is easily

TABLE III

$COCl_2$	d(CO)/dt	Absorption, %	$COCl_2$	d(CO)/dt	Absorption, %
2.90	0.060	20.0	23.74	0.211	83.5
5.73	.096	35.5	26.75	.233	86.9
8.74	.124	48.5	29.82	.220	89.6
11.80	.156	59.2	32.65	.240	91.6
14.70	.175	67.3	35.80	.250	93.4
20.68	.211	79.2			

explained as follows. From the exponential character of Beer's law it is known that strict proportionality between the amount of light absorbed and the concentration of the absorbing substance exists only for low absorption, *i. e.*, low concentrations. When the amount of absorption is large, this proportionality breaks down, the amount of absorption increasing more and more slowly as the concentration increases. Hence photochemical reactions which are first order with respect to the amount of light absorbed tend to become zero order with respect to the absorbing substance at high concentrations where absorption becomes large. This is exactly the case here. In connection with the work on the quantum yields of the phosgene reactions, the absorption coefficients of phosgene were measured in the predissociation region. Thus it is possible to calculate the percentage absorption, which, unlike the phosgene pressure, should be proportional to the initial rate. This has been done in column 3 of Table III, assuming a value of the absorption coefficient $\epsilon = 0.011$, where ϵ is defined by the equation $\log (I_0/I) = pl\epsilon$, the units of p being in cm. and l in cm. ($l = 3.0$). From this equation the percentage absorption can be calculated by Percentage Absorption $= [(I_0/I) - 1]/(I_0/I)$. The value taken for ϵ is that corresponding to $\lambda = 2537$ Å., the most intense Hg line beyond the predissociation limit.

If the initial rates of Table III are plotted against the corresponding percentage absorption calculated in the above manner, a straight line is obtained, clearly indicating that the rate is a function of the first power of the light absorbed.

In Table IV are summarized the results of a series of experiments in which the effect of variation of the incident light intensity, by means of a set of calibrated screens, was investigated.

TABLE IV

Transmission, %	100.0	69.5	48.6	38.0	29.7	15.6
Rate	0.080	0.057	0.038	0.029	0.027	0.013
Δ	− .002	.000	− .002	− .003	+ .003	+ .002

The third column of the Table shows the deviations from linearity (*i. e.*, from the best straight line through the points). As might have been predicted from the phosgene results, the rate is a linear function of the incident intensity.

From the above results it appears that the rate is much more sensitive to the amount of light absorbed than to the hydrogen pressure. If d(CO)/dt = $kI_{\text{abs.}}$ = $kI_0(COCl_2)$, we may write d(CO)/dt = $-$d($COCl_2$)/dt = $kI_0(COCl_2)$, or, $-$d log ($COCl_2$)/dt = k'. If, therefore, the rate law were the simple first order expression above, the change in the logarithm of the ($COCl_2$) per unit time might be expected to remain constant. That this is not so is shown by the results of Table V. δ is the rate of change of the log ($COCl_2$).

TABLE V

Time, minutes	3	6	10	15	20	25	30	35
δ	0.015	0.013	0.013	0.011	0.009	0.009	0.009	0.007

Time, minutes	45	55	65	75	85	100
δ	0.007	0.005	0.005	0.004	0.003	0.003

(71% completion)

In order to investigate the cause of this deviation from the first order law, further series of experiments were undertaken. In Table VI are shown the results of some experiments in which the effect of total pressure was investigated. ($COCl_2$), (H_2), and the incident light intensity were kept constant and total pressure varied by the addition of (CO_2).

TABLE VI

CO_2, cm.	0.0	10.0	15.0	20.0	25.1	40.1	45.2
Relative rate	1.000	0.909	0.871	0.841	0.775	0.630	0.594
Δ	0.000	− .005	.000	+ .015	− .005	− .015	− .005

The rate appears to be inversely proportional or at least involves a term which is inversely proportional to the first power of the total pressure. A series of experiments in which nitrogen was the added gas yielded quite similar results.

Next, a series of experiments was made in which carbon monoxide was added to the reaction gases in varying amounts. The results appear in Table VII.

TABLE VII

CO, cm. H_2SO_4	0.00	10.09	15.07	21.35	34.91
Relative rate	1.000	0.757	0.722	0.666	0.595

It is evident that the inverse effect on the rate is much more pronounced with carbon monoxide than with carbon dioxide (or nitrogen). Furthermore, when the relative rate is plotted against the carbon monoxide pressure, a distinct curvature is observed so that the curve resembles the graph of an inverse square function. This must be interpreted as due to the fact that carbon monoxide, apart from its total pressure effect, has a specific effect as well in lowering the rate. This means that carbon monoxide probably enters the rate law explicitly.

In the following table the values of δ have been tabulated for a series of three experiments. Expt. A was a "control" reaction showing the usual falling off of δ. In Expt. B hydrogen was added during the reaction and in Expt. C there was a large excess of carbon monoxide present. In other respects the conditions were identical in the three experiments ($P_{H_2} = P_{COCl_2} = 10$ cm. H_2SO_4).

TABLE VIII

A		B		C	
t, mins.	δ	t, mins.	δ	t, mins.	δ
15	0.082	10	0.077	10	0.038
25	.069	20	.067	20	.038
35	.066	30	.061	30	.036
45	.063	40	.063[a]	40	.042
55	.058	50	.064	60	.041
65	.057	60	.075[b]	80	.038
75	.052	70	.081	100	.039
85	.047				

[a] 5 Cm. H_2SO_4 of H_2 added. [b] 27 Cm. H_2SO_4 of H_2 added.

The above experiments and other similar ones seem to indicate that the amount of deviation from first order may depend upon the value of the ratio $H_2/(CO)(M)$. By alternate additions of hydrogen and carbon monoxide, it was found possible to vary the deviation almost at will. It is further evident that fairly constant values of δ may be obtained by maintaining an excess of hydrogen as in "B" or by adding a large excess of carbon monoxide as in "C."

Discussion

It has been possible to derive a rate law in formal agreement with the above experimental facts from the following reaction mechanism

$$COCl_2 + h\nu \longrightarrow COCl + Cl \qquad (1)$$
$$Cl + H_2 \longrightarrow HCl + H \qquad (2)$$
$$H + COCl_2 \longrightarrow CO + Cl + HCl \qquad (3)$$
$$CO + Cl + M \longrightarrow COCl + M \qquad (4)$$
$$2COCl \longrightarrow COCl_2 + CO \qquad (5)$$

The rate of reaction according to this reaction scheme is given by

$$d(CO)/dt = k_3(H)(COCl_2) + k_5(COCl)^2 - k_4(CO)(Cl)(M)$$

Assuming that the rates of change of (COCl), (Cl), and (H) are negligibly small compared to their rates of formation and disappearance, we may write

$$d(COCl)/dt = I_{abs.} + k_4(CO)(Cl)(M) - k_5(COCl)^2 = 0 \qquad (I)$$
$$d(Cl)/dt = I_{abs.} - k_2(Cl)(H_2) + k_3(H)(COCl_2) - k_4(CO)(Cl)(M) = 0 \qquad (II)$$
$$d(H)/dt = k_2(Cl)(H_2) - k_3(H)(COCl_2) = 0 \qquad (III)$$
$$I + II + III = 0 = 2I_{abs.} - k_5(COCl)^2$$
$$\text{or, } k_5(COCl)^2 = 2I_{abs.} \qquad (IV)$$

From II we obtain

$$k_3(H)(COCl_2) - k_4(CO)(Cl)(M) = k_2(Cl)(H_2) - I_{abs.}$$

Substituting the right-hand member in the expression for the rate of reaction we have

$$d(CO)/dt = k_2(Cl)(H_2) - I_{abs.} + k_5(COCl_2)^2 \qquad (V)$$

According to IV this becomes

$$d(CO)/dt = k_2(Cl)(H_2) + I_{abs.} \quad (VI)$$

From I we obtain

$$k_4(CO)(Cl)(M) = I_{abs.}, \text{ or}$$
$$(Cl) = I_{abs.}/k_4(CO)(M) \quad (VII)$$

Substitution of VII in VI gives

$$d(CO)/dt = I_{abs.} + k_2 I_{abs.}(H_2)/k_4(CO)(M) \quad (VIII)$$
$$= I_{abs.}\left[1 + \frac{k_2(H_2)}{k_4(CO)(M)}\right]$$

Since in most of the experimental work the total absorption was small we may make the substitution $I_{abs.} = I_0(COCl_2)$, which reduces VIII to

$$d(CO)/dt = I_0(COCl_2)\left[1 + \frac{k_2(H_2)}{k_4(CO)(M)}\right]$$

an equation in formal agreement with and capable of explaining the experimental facts.

It may be remarked that a rate law of this form indicates an infinite initial rate of reaction (since carbon monoxide is one of the reaction products). This, of course, is not observed. In every case, however, where carbon monoxide is not added before the start of the reaction, the first two or three values of δ are invariably noticeably larger than succeeding values. The second term thus makes its largest contribution to the rate at the start of the reaction. The fact that the ratio $H_2/(CO)(M)$ decreases so rapidly as reaction proceeds explains the rapid falling off of the δ values.

Special notice should be taken of the manner in which (M) enters the rate law, as any molecule which is capable of taking up the excess energy of, and so stabilizing, the intermediate COCl. In the case of the photochemical formation of phosgene, Lenher and Rollefson[3] identified (M) with (Cl_2) and this was later confirmed on theoretical grounds by Rollefson and Eyring.[4] The possibility of Cl_3 molecules (such as they postulated) reacting with CO to form COCl is indeed remote in the phosgene-hydrogen reaction since no Cl_2 is present. Hence it is difficult to identify (M) with any particular molecular species in our present case. Furthermore, it is undoubtedly incorrect to assume that all the kinds of molecules present are equally capable of stabilizing COCl and thus tacitly to assume the identity of (M) and the total pressure. It is well known from the study of the extinction of fluorescence that molecules differ greatly in their efficiency in taking up energy. In confirmation of this, carbon monoxide was found to have a more pronounced "total pressure" effect than nitrogen. For this reason, (M) should probably be written $(M) = a\,(COCl_2) + b\,(H_2) + c\,(CO) + d(HCl)$, where the coefficients are "stabilizing efficiencies." It is this indeterminate character of (M) which makes a more rigorous analytical test of the rate law impossible.

(3) Lenher and Rollefson, THIS JOURNAL, **52**, 500 (1930).

(4) Rollefson and Eyring, *ibid.*, **54**, 170 (1932).

In the reaction mechanism, no reaction has been postulated between COCl and H_2 to form, possibly, COH, since there was no evidence of formaldehyde formation, which might be supposed to take place through this latter intermediate. As a consequence COCl may be supposed to build up sufficient concentration to bring about the chain terminating step

$$2COCl \longrightarrow COCl_2 + CO \qquad (5)$$

This step is thus fairly consistent with the other partial reactions of the mechanism.

Summary

The quantum yields have been measured for the photochemical oxidation of phosgene, the phosgene-sensitized oxidation of carbon monoxide, and the photochemical reaction of phosgene with hydrogen. The results confirm the rate mechanisms proposed for these three reactions.

The photochemical reaction between phosgene and hydrogen: $COCl_2 + H_2 \longrightarrow CO + 2HCl$, has been studied. The rate of the reaction has been investigated and a mechanism devised from which the theoretical rate law

$$\frac{d(CO)}{dt} = kI_0(COCl_2)\left[1 + \frac{k_2(H_2)}{(CO)(M)}\right]$$

may be derived. It has been shown that this expression is in essential accord with the experimental facts. The reaction rate has been discussed from the standpoint of this rate law and various experimental points explained. The absence of formaldehyde formation, it has been pointed out, is probably due to the non-reactivity of COCl toward H_2. This non-reactivity in turn is believed to cause an increase in the concentration of COCl so that $2COCl \longrightarrow COCl_2 + CO$ becomes the chain terminating process.

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The Phosgene-Sensitized Oxidation of Carbon Monoxide

By G. K. Rollefson and C. W. Montgomery

As the result of a number of investigations concerned with the inhibiting effect of oxygen on the photosynthesis of phosgene[1,2,3,4] it has been shown that at high oxygen pressures the phosgene formation becomes negligibly small, the chlorine-sensitized oxidation of carbon monoxide being predominant. In the various mechanisms proposed for this reaction[5] the formation of carbon dioxide is believed to take place through the action of oxygen on the intermediate COCl. It has previously been shown that in the case of the direct photochemical oxidation of phosgene[6] this same intermediate is produced by the action of ultraviolet light on phosgene, and evidence has been submitted that the same state obtained in such a system as is produced by the action of visible light on a mixture of chlorine, carbon monoxide and oxygen. It is therefore to be expected that the oxidation of carbon monoxide might be sensitized by phosgene in a manner entirely analogous to the chlorine-sensitized reaction. Such has been found to be the case and the reaction has been studied in the hope of arriving at a comparison with the chlorine-sensitized oxidation.

Experimental

The apparatus employed in the kinetic study was, in general, the same as that previously described for the work on the direct oxidation of phosgene.[6] The same cylindrical quartz reaction vessel was used with the same method of water cooling. The source of illumination was the full light of a 220-volt Cooper–Hewitt quartz mercury arc.

The phosgene (Kahlbaum) was distilled from a glass bomb and was purified in the manner previously described. Oxygen was prepared electrolytically, purified and dried as before.[6] Carbon monoxide was generated by heating a mixture of concentrated sulfuric and formic acids, washed in a bubbler containing strong sodium hydroxide solution, and dried in a similar bubbler containing concentrated sulfuric acid. The three gases were stored in three three-liter bulbs from which they could be admitted to the reaction vessel as needed.

The reaction was followed by means of a sulfuric acid (sp. gr. 1.84) manometer or a mercury manometer (with the mercury surface protected by 3 or 4 cm. of sulfuric acid) depending on the total pressures of the gases used. Due to the large Draper effect produced by the reaction, before readings were taken the light from the arc was cut off from the reaction vessel by means of a shutter and the pressure allowed to reach a constant value.

In several of the experiments, in order to check the stoichiometry of the reaction, pressure readings were taken both at room temperature and at

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(1) Chapman and Gee, *J. Chem. Soc.*, **99**, 1726 (1911).

(2) Bodenstein, *Sitzber. preuss. Akad. Wiss.*, **13**, 104 (1926).

(3) Schumacher, *Z. physik. Chem.*, **129**, 241 (1927).

(4) (a) Rollefson, *Trans. Faraday Soc.*, **27**, 465 (1931); (b) This Journal, **52**, 3562 (1930); (c) **55** 148 (1933).

(5) Lenher and Rollefson, *ibid.*, **52**, 500 (1930).

(6) Rollefson and Montgomery, *ibid.*, **55**, 142 (1933).

liquid air temperature. From these two sets of readings, the amount of sensitized oxidation according to the reaction

$$2CO + O_2 \longrightarrow 2CO_2 \qquad (1)$$

and the amount of direct oxidation of phosgene according to

$$2COCl_2 + O_2 \longrightarrow 2CO_2 + 2Cl_2 \qquad (2)$$

were calculated. This was done by means of the relations

$$\Delta P_1 = (\Delta P_R + \Delta P_A)/4; \ \Delta P_2 = -\Delta P_R + \Delta P_1$$

where ΔP_1 is the pressure change due to reaction (1), ΔP_2 is the pressure change due to reaction (2), ΔP_R the over-all pressure change at room temperature, and ΔP_A the over-all pressure change at liquid air temperature converted, by means of an empirical "freeze-out" factor, which was determined for each run, to the corresponding pressure change at room temperature. In all the runs made, the sensitized reaction went to completion according to equation (1) and was so rapid relative to reaction (2) that direct phosgene oxidation could be neglected until (1) was approximately 80% complete.

Results

In Table I are summarized the results of five experiments in which the $COCl_2$ pressure was varied from 2.45 to 20.00 cm. of sulfuric acid, the other variables being kept constant. The fourth column indicates the linearity between rate and the square root of the $COCl_2$ pressure.[7]

TABLE I

$(COCl_2)$	2.45	5.02	10.00	14.45	20.00
$(COCl_2)^{1/2}$	1.57	2.24	3.16	3.80	4.47
$d(CO_2)/dt$	1.00	1.47	1.93	2.40	2.80
$(d(CO_2)/dt)/(COCl_2)^{1/2}$	0.637	0.656	0.611	0.632	0.626

In Table II are summarized the results of a series of experiments in which the incident light intensity was varied by means of a set of calibrated screens. In the table, the intensity with no screen is taken as 100. The rate is seen to be fairly definitely a function of the square root of the incident intensity, in agreement with the previous results on the $COCl_2$ dependence. The fourth column of the table indicates the deviation from linearity, values of Δ being obtained from the best straight line through the points.

TABLE II

I_0	100.0	67.0	47.0	37.9	29.0	5.9
$I_0^{1/2}$	10.0	8.2	6.9	6.2	5.4	2.4
$d(CO_2)/dt$	0.56	0.47	0.36	0.34	0.29	0.12
Δ	+0.010	+0.020	−0.015	0.000	0.000	−0.010

Table III gives the results of a series of experiments in which the carbon monoxide pressure alone was varied. Plotting the rate against the square root of the carbon monoxide pressure yields a straight line indicating the dependence on the square root of the carbon monoxide pressure. In several experiments at very low carbon monoxide pressures, the rate falls away from this square root relationship. In these cases, however, the rate of oxidation of carbon monoxide is so much slower that the rate of direct oxidation of phosgene is no longer negligible in comparison. Since this direct oxidation leads to a pressure change in the opposite direction, the effect produced is to cause an anomalous lowering of the rate of the sensitized reaction.

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[7] In these and the following results, the pressure has been left in terms of cm. of mercury or sulfuric acid and the rate expressed in cm. of mercury or sulfuric acid per minute.

TABLE III

(CO)	$(CO)^{1/2}$	$d(CO_2)/dt$
14.02	3.32	5.12
18.39	4.29	6.60
27.85	5.28	8.92
37.32	6.20	10.36
47.07	6.86	11.62
56.98	7.55	12.08
66.65	8.15	13.40
76.22	8.73	14.60
86.15	9.28	15.40

TABLE IV

Δ	(O_2)	$d(CO_2)/dt$
−0.40	1.47	1.15
− .50	3.24	1.62
+ .20	5.05	2.00
+ .05	6.94	2.07
+ .25	10.87	2.35
− .50	15.62	2.45
− .05	20.70	2.40
+ .10	27.40	2.50
.00	36.25	2.40

It was further necessary to investigate the dependence of the rate on the oxygen pressure, in order to afford a closer comparison with the chlorine sensitized reaction. In the latter reaction it has been shown that the rate although dependent on the oxygen pressure at low pressures, becomes independent of it as the pressure is increased. In Fig. 1 and Table IV are presented the results of a series of experiments in which the oxygen pressure was varied between 1.5 and 36 cm. ($COCl_2$, 5 cm., CO, 10 cm.). The rate obviously becomes independent of the oxygen pressure at approximately 15 cm. pressure. In order to test the oxygen dependence in the region where the curve bends down to the origin, several low pressure experiments were made, the results of four of which are shown in Table V.

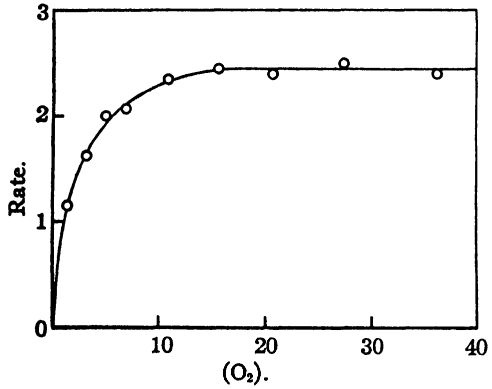

Fig. 1.

TABLE V

(O_2)(cm. H_2SO_4).......	1.73	3.75	6.45	9.30
$(O_2)^{1/2}$...............	1.16	1.94	2.54	3.05
$d(CO_2)/dt$............	2.56	4.28	5.72	6.80
$(d(CO_2)/dt)/(O_2)^{1/2}$....	2.21	2.20	2.25	2.23

In this low oxygen region, it is evident that the rate is a function of the square root of the oxygen pressure.

On the basis of the above experiments, the reaction appears to fall into two fairly definite pressure ranges in which the rate laws are different. For low oxygen pressures the rate may be represented by the equation

$$d(CO_2)/dt = KI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}(O_2)^{1/2} = kI_{abs.}^{1/2}(CO)^{1/2}(O_2)^{1/2} \qquad (1)$$

(where the substitution $I_{abs.} = I_0(COCl_2)$ is justified by the low light absorption), while at higher oxygen pressures, the oxygen dependence disappears, the rate law becoming

$$d(CO_2)/dt = kI_{abs.}^{1/2}(CO), \qquad (2)$$

This change of order was confirmed by the results of two series of experiments in which the phosgene pressure and light intensity were kept constant and the carbon monoxide and oxygen pressures were kept in constant ratio but their total pressure varied. Under these conditions, the rate should be proportional to the total pressure (carbon monoxide and oxygen) in the region where equation (1) holds, but should fall off from this proportionality in the region of equation (2). The data are presented in Tables VI and VII. The correctness of the above statements is clearly evident in the small deviations from linearity (Δ) in Table VI and the increasingly large deviations in Table VII.

TABLE VI (LOW PRESSURE O_2)

$(O_2 + CO)$(cm. H_2SO_4)	$d(CO_2)/dt$	Δ
10.10	1.9	−0.50
20.66	4.7	.00
40.78	10.0	+ .75
60.55	13.6	.00
80.35	18.1	.00

TABLE VII (HIGH PRESSURE O_2)

$(O_2 + CO)$(cm. Hg)	$d(CO_2)/dt$	Δ
8.0	0.73	0.00
16.0	1.43	− .05
24.0	2.13	− .08
32.0	2.77	− .20
40.0	3.05	− .60

In order to obtain a clearer confirmation of this change of order and the independence of the rate on the oxygen pressure at higher pressures, as well as of the square root relation at low pressures, the data of Table IV have been treated in the following manner. In this series of experiments, the rate is a function of the oxygen pressure alone, the other variables of the system being kept constant. The rate may therefore be represented by the equations

$$d(CO_2)/dt = k(O_2)^{1/2} \qquad (1)$$

for low oxygen pressures, and

$$d(CO_2)/dt = k' \qquad (2)$$

at higher oxygen pressures. Taking the logarithms of both sides of these equations we obtain

$$\log d(CO_2)/dt = \log k + {}^1/_2 \log (O_2) \qquad (1')$$

and

$$\log d(CO_2)/dt = \log k' \qquad (2')$$

If, therefore, we plot the logarithm of the rate against the logarithm of the oxygen pressure, we should obtain a straight line of slope 0.5 for low oxygen pressures and a straight line parallel to the log (O_2) axis at higher pressures. This was done for the data of Table IV and the expected results obtained. In Fig. 2 d log rate/d log (O_2), *i. e.*, the slopes of the log rate *vs.* log (O_2) plot, are plotted against log (O_2). The low and high pressure (O_2) regions are clearly indicated as well as the transition range.

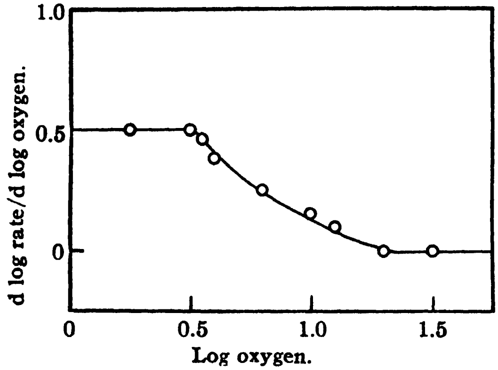

Fig. 2.

The quantum yield[8] has been found to be approximately 100 at pressures of about 40.0 mm. of $COCl_2$, CO and O_2. Schumacher[3] measured the quantum yield of the chlorine-sensitized oxidation and found it to be roughly of the order of magnitude of 1000 molecules per quantum for pressures of (CO) = (Cl_2) = $^1/_2$ atmosphere and O_2 = 1000 mm., in the region of maximum chlorine absorption. If we assume that the rate law which Schumacher found, *i. e.*

$$d(CO_2)/dt = kI_0^{0.71}(Cl_2)^{0.71}(CO)^{1/2} = kI_{abs.}^{0.71}(CO)^{1/2}$$

becomes, at lower chlorine pressures

$$d(CO_2)/dt = kI_0(Cl_2)(CO)^{1/2} = kI_{abs.}(CO)^{1/2}$$

as has been shown by Rollefson,[4b,5] we may obtain a formal expression for the quantum yield by dividing this equation by $I_{abs.}$ thus

$$\gamma = (d(CO_2)/dt)/I_{abs.} = k(CO)^{1/2}$$

At lower pressures of chlorine, the quantum yield should then be only a function of the square root of the carbon monoxide pressure. By a simple calculation we find the quantum yield of the chlorine-sensitized oxidation for a carbon monoxide pressure equal to that (4 cm. of carbon monoxide) at which the quantum yield of the phosgene sensitized oxidation was measured, to be

$$\gamma = \sqrt{40}\cdot 1000/\sqrt{380} \sim 300$$

The quantum yields of the phosgene-sensitized and chlorine-sensitized reactions are thus seen to be of approximately the same magnitude.

Discussion

From the data presented above, it is evident that at low oxygen pressures the rate of oxidation of carbon monoxide may be expressed by the equation

$$d(CO_2)/dt = kI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}(O_2)^{1/2}$$

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[8] The experimental details will be published soon in connection with the determination of the quantum yields of some other reactions.

while at high oxygen pressures ($P_{O_2} > 15$ cm.) the rate becomes independent of the oxygen. As expected, the phosgene-sensitized oxidation appears to be quite similar to the chlorine-sensitized reaction. The fact that the quantum yields are of the same magnitude indicates, of course, that the chain lengths of the two reactions are the same. This gives further confirmation to the view expressed previously that there is no essential difference between the system: phosgene, carbon monoxide, and oxygen illuminated with ultraviolet light of frequency corresponding to the phosgene predissociation region, and the system: chlorine, carbon monoxide, and oxygen illuminated with visible light of frequency corresponding to the region of the chlorine absorption continuum. The similarity in the two systems is further shown by the manner in which the carbon monoxide pressure enters the rate laws of both reactions and by the fact that both reaction rates appear to involve oxygen explicitly at low oxygen pressures and become independent of it at higher pressures.[9] The only interpretation of these facts probably is that both the carbon monoxide and oxygen play identical roles in the rate mechanisms of the two reactions.

Another point of analogy between the two systems is evident in the manner in which the rate depends upon the intensity of light absorbed. A significant difference also exists, however. It has been shown[11] that, in the case of the chlorine-sensitized reaction, the rate at low chlorine pressures is proportional to the light absorbed while at higher pressures it becomes proportional to the square root of the light absorbed. In the intermediate range such exponents as Schumacher's $I_{\text{abs.}}^{0.71}$ are found. This change of function with pressure has been most plausibly explained by assuming two different methods of recombination of the chlorine atoms produced by the light. At low pressures destruction of the chlorine atoms by collision with impurities or the reaction vessel walls is greater, while at higher pressures recombination is brought about predominantly by second order collisions in the gas phase. In the case of the phosgene-sensitized oxidation no such change is found in the dependence of the rate on the light absorbed, the rate remaining proportional to the square root of the light absorbed. Reasoning by analogy, this can be interpreted by assuming the predominance throughout the range studied of some homogeneous second order chain terminating process corresponding to the disappearance of chlorine atoms in the chlorine-sensitized reaction. On the basis of the mechanism of Lenher and Rollefson this would be $COCl + Cl \longrightarrow CO + Cl_2$.

A satisfactory derivation of the rate law from any mechanism yet devised has not been obtained. The derived equations either give the wrong

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(9) The dependence of the rate of the chlorine sensitized reaction at low oxygen pressures on the oxygen has not been determined quantitatively as the phosgene formation predominates under such conditions. In that case the amount of carbon dioxide formed in a given time is determined by the law governing the division of the carbon monoxide between the two competing reactions, whereas in the system we are discussing in this paper the reaction between carbon monoxide and oxygen can be considered to be the only one occurring.

exponents for the factors involved or else do not, in the limit of high oxygen pressures, yield an expression independent of the oxygen. Likewise no satisfactory derivation has yet been made of the rate law for the chlorine-sensitized reaction. Recently Warming[10] has shown that the mechanism of Schumacher[11] is thermodynamically unsound. There can be but little question, in the light of the experimental results obtained, that practically the same mechanism will be found to fit both the chlorine-sensitized and the phosgene-sensitized reactions, with the exception of the primary process, which in the phosgene reaction must be $COCl_2 + h\nu \longrightarrow COCl + Cl$. After this initial process, it is to be expected that oxygen and carbon monoxide will take part in the same reactions in the reaction chains of both sensitized oxidations. In devising a mechanism, the principal difficulty appears to be to get a set of partial reactions the rate law of which will involve the square root of the oxygen at low oxygen pressures and will become independent of oxygen at higher pressures. It has been found possible, however, to set up the following mechanism from which the low pressure rate law may be derived.

$$COCl_2 + h\nu \longrightarrow COCl + Cl \quad (1)$$
$$CO + Cl + M \longrightarrow COCl + M \quad (2)$$
$$COCl + O_2 \longrightarrow CO_3Cl \quad (3)$$
$$CO_3Cl + CO \longrightarrow 2CO_2 + Cl \quad (4)$$
$$CO_3Cl + COCl \longrightarrow 2CO_2 + Cl_2 \quad (5)$$

This mechanism leads to the rate law

$$d(CO_2)/dt = 2I_{abs.} + kI_{abs.}^{1/2}(CO)^{1/2}(O_2)^{1/2}$$

which, considering the large value of the quantum yield, reduces to

$$d(CO_2)/dt = kI_{abs.}^{1/2}(CO)^{1/2}(O_2)^{1/2}$$

the low oxygen pressure experimental rate law. The assumption of CO_3Cl in the above mechanism presents nothing contradictory to the mechanism already given for the direct photochemical oxidation of phosgene (8), since in that mechanism process (3) as written above is kinetically identical to $COCl + O_2 \longrightarrow CO_2 + ClO$. CO_3Cl may, perhaps, be regarded as a reactive peroxide of the sort postulated by Bodenstein.[12] In the high pressure region it is conceivable that oxygen inhibits the oxidation as has been observed in other cases.[12] This might be brought about through the action of oxygen at some stage following reaction (3), resulting in a process which would terminate the chain. Except for this effect this system is in perfect agreement with the other reactions for which the intermediate COCl has been postulated and must be considered as additional evidence for the existence of that substance.

Summary

A kinetic study of the phosgene-sensitized oxidation of carbon monoxide has been made. The rate law for low pressures of oxygen has been shown

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(10) Warming, *Z. physik. Chem.*, **B18**, 156, 158 (1932).

(11) Schumacher and Stieger, *ibid.*, **B18**, 169 (1931).

(12) Bodenstein, *Sitzber. preuss. Akad. Wiss.*, 73–88 (1931).

to be: $d(CO_2)/dt = kI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}(O_2)^{1/2}$, and for higher oxygen pressures: $d(CO_2)/dt = kI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}$. As in the case of the chlorine-sensitized oxidation of carbon monoxide, it has not yet been possible to develop a mechanism for the reaction capable of explaining the experimental rate law over the whole range. The two reactions have been compared and have been found to be very similar in several important respects. It has been concluded, therefore, that probably very similar mechanisms will be found to apply to both chlorine- and phosgene-sensitized oxidations.

BERKELEY, CALIFORNIA RECEIVED JUNE 10, 1933
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[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

The Reduction by Hydrogen and the Thermal Decomposition of Nitrides Made by the Reaction of Ammonia with Various Promoted and Unpromoted Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND KATHARINE S. LOVE

Phase rule investigations[1] have in the last few years shown that at least two nitrides of iron are formed by passing ammonia over iron in the temperature range 400 to 525°. At 450° and one atmosphere pressure, for example, an ammonia–hydrogen mixture containing between 30 and 70% ammonia will convert the iron into a body-centered cubic nitride whose composition is close to that of Fe_4N; ammonia percentages ranging from 70 to 100% will convert the Fe_4N into an hexagonal nitride whose composition varies with the percentage of ammonia from one approximating Fe_3N to one that closely corresponds to Fe_2N. As a part of a study being made of the mechanism by which iron catalysts are able to effect the synthesis of ammonia, the rates and nature of the decomposition and of the reduction by hydrogen of the various nitrides, prepared both from active and from inactive iron ammonia catalysts, have been determined.

Experimental

The various nitrides were prepared by passing suitable ammonia–hydrogen mixtures at about 400° over finely divided iron synthetic ammonia catalysts obtained by the reduction in hydrogen of fused Fe_3O_4. Portions of each nitride preparation were analyzed by a modified Kjeldahl method; usually samples were also taken for x-ray photographs. Table I gives the composition of the samples and in some cases the nature of their x-ray pattern. Samples for both x-ray and chemical analysis were obtained in an oxygen-free nitrogen atmosphere.

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[1] Emmett, Hendricks and Brunauer, THIS JOURNAL, **52**, 1456 (1930); Lehrer, *Z. Elektrochem.*, **36**, 383 (1930); Eisenhut and Kaupp, *ibid.*, **36**, 392 (1930); Lehrer, *ibid.*, **36**, 460 (1930); Brunauer, Jefferson, Emmett and Hendricks, THIS JOURNAL, **53**, 1778 (1931).

TABLE I

COMPOSITION OF IRON NITRIDE SAMPLES

Designation of nitride	Source of iron from which the nitride was made[a]	Nitrogen in sample, %[b]	X-Ray analysis
A-1	Cat. 973	5.91	Only Fe_4N lines
A-2	Cat. 973	11.00	Only Fe_3N-Fe_2N lines
B-1	Cat. 984	6.04	Only Fe_4N lines
B-2	B-1	10.81	
B-3	Cat. 984	7.53	Fe_3N-Fe_2N 50% Fe_4N 50%
B-5	Cat. 984*	5.64	
C-1	Cat. 921	6.02	Only Fe_4N lines
C-2	C-1[c]		
D-1	Cat. 920	6.01	Only Fe_4N lines
D-2	Cat. 920*	7.89	
D-3	D-2	6.02	
E-1	Iron oxalate[d]		

[a] The samples designated by * were 8–14 mesh; all others were ground to pass a 200-mesh screen. The catalysts were obtained by the reduction in hydrogen of variously promoted fused magnetites: 984 contains 2.92% Al_2O_3 and 1.05% K_2O; 921, 1.05% Al_2O_3; 920, 0.2% K_2O; 973, 0.15% Al_2O_3. [b] The formula Fe_4N corresponds to 5.90% nitrogen; Fe_2N, to 11.14% nitrogen. [c] C-1 was flushed with N_2 at 100° for two hours. [d] This Fe_4N sample was made by Mr. Brunauer and used by him in phase rule studies.

The decomposition experiments were carried out in an all-glass apparatus, the evolved nitrogen being measured in a gas buret at about atmospheric pressure. The furnace used was fitted with an aluminum block. When once adjusted the furnace could be kept at a given temperature by controlling it with hand rheostats, the variation being about 2° during a decomposition run. The experimental uncertainty in each determination of the amount of nitrogen evolved per five minutes per gram of iron was about 0.03 cc.

The reduction experiments were carried out by bringing the nitride samples to the desired temperature in a stream of nitrogen and then quickly replacing the nitrogen with pure hydrogen. The exit gas was analyzed continually for ammonia.

Results on the Thermal Decomposition of the Nitrides of Iron

(a) Fe_4N Decomposition.—The general nature of the decompositions of the various Fe_4N samples can be judged from the types of curves shown in Fig. 1. The decompositions seem to be autocatalytic, the rates being low at first and increasing as a function of time. One peculiar exception to this rule was noted. The decomposition rate of the Fe_4N made from a doubly promoted catalyst was in a certain temperature range practically independent of the nitrogen content of the sample. This is illustrated in a run on sample B-3, Fig. 1. The first portion of the curve represents the decomposition of a little Fe_3N known to be present. The rate of nitrogen evolution after the sample had attained a composition corresponding to Fe_4N was practically constant at 0.28 to 0.32 cc. of nitrogen per g. of Fe for about thirteen hours; when about 95% of the nitrogen had been evolved the rate decreased rapidly, dropping from 0.3 cc. to less than 0.01 cc. per five minutes per gram of Fe in about one and one-half hours. This zero order solid decomposition made possible the determination of the temperature coefficient of nitrogen evolution from Fe_4N.

Temperature coefficients were determined on four Fe_4N samples, three of them being taken from nitride preparation B-1 and the fourth from an 8–14 mesh sample designated as B-5. The logarithms of the rates of decomposition in these temperature coefficient runs are shown plotted against $1/T$ in Fig. 2. Each point on these curves represents an hour's decomposition run at a given temperature; no change in rate was observed in any of these cases during the hour's run. It is evident however that the temperature coefficient calculated by going back from a higher to a lower temperature is considerably smaller than that obtained by going from a lower to a higher temperature. Thus in run 26 the slope of the line connecting points a, b and c corresponds to 69,000 calories and that connecting points d, e and f, 52,000 calories; however, one connecting points c and d indicates an energy of activation of only 42,000 calories. The real energy of activation of the decomposition is apparently between the two extreme values. From the combined results it is concluded that the energy of activation for the reaction $Fe_4N = 4Fe + 1/2N_2$ is about 50,000 calories.

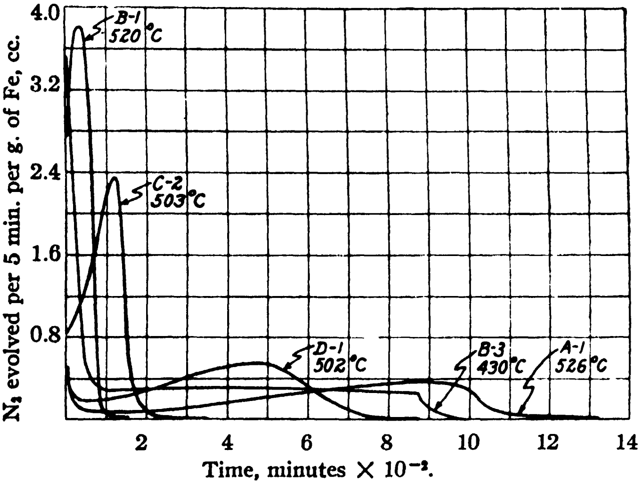

Fig. 1.—Rate of decomposition of Fe_4N prepared from various iron synthetic ammonia catalysts.

In the course of the experiments on thermal decomposition it became evident that some unknown factor was causing the rate of decomposition of the Fe_4N made from doubly promoted catalysts to vary from run to run. In particular, it became evident that the first run (always made within twenty-four hours after preparing the Fe_4N sample) gave higher results than any of the succeeding runs. The cause of this decrease after the initial run was not satisfactorily ascertained. Increased precautions in excluding possible traces of water vapor and of oxygen from the sample during its storage after the first run seemed to decrease the effect; however, it was still very much in evidence in the last few experiments made. To illustrate the magnitude of the disturbing factor and at the same time show the relative approximate rates of decomposition of the various nitrides studied, the logarithms of the maximum rates observed are plotted against $1/T$ in Fig. 2. It must of course be borne in mind that only in the case of the zero order decompositions of the doubly promoted sample is such a method of comparing rates quantitative. Runs 36, 38 and 13 on sample B were all "first runs," as was also run 41 on sample D; a comparison of the rates in these four runs indicates that Fe_4N prepared from an active synthetic ammonia catalyst, B, decomposes much more rapidly than that made from a comparatively inactive catalyst, D. Unfortunately the runs on the pure iron catalyst (2 and 4, Fig. 2) and on the catalyst promoted with Al_2O_3 (10 and 11, Fig. 2) are either "second" runs or made several days after the preparation of the samples. Hence rate comparisons involving these two last catalysts are not warranted. The decomposition of the Fe_4N made from iron obtained by the reduction of ferric oxalate was by far the slowest of all nitride samples tried (Run 6).

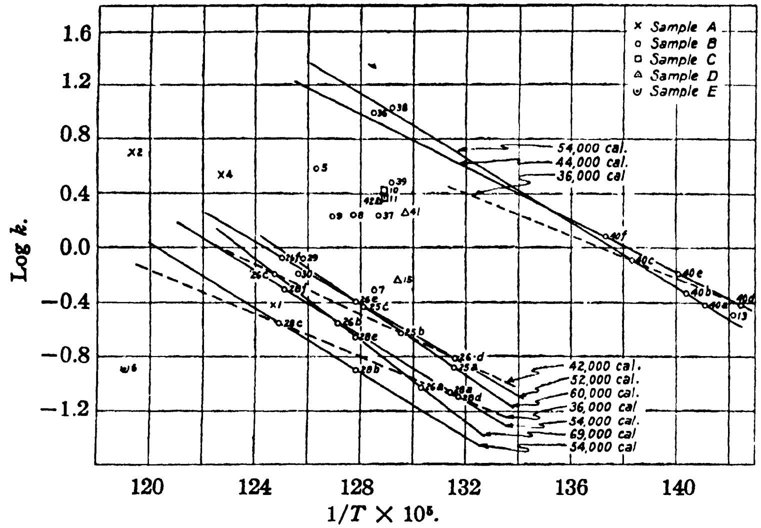

Fig. 2.—Variation of the rate of decomposition of Fe_4N with the temperature and with the type of catalyst used as a source of iron. The temperature coefficient of Fe_4N decomposition as determined by runs 25, 26, 28 and 40 is expressed in terms of the energy of activation, E, involved in the decomposition.

Since it appeared that traces of poison might affect the rate of decomposition of the nitrides quite appreciably, a few experiments were made in which poisons were deliberately added to the nitrides and the effect on the rate noticed. The addition of about 0.2 cc. of either hydrogen sulfide or oxygen to the doubly promoted Fe_4N sample at the end of run 28 produced no appreciable change in rate; however, an additional 1.3 cc. of hydrogen sulfide caused the rate to drop immediately from 0.25 to 0.014 cc. per five-minute period.

(b) **Fe_2N Decomposition.**—Typical decomposition curves for Fe_2N samples are shown in Fig. 3. The decomposition is of a non-autocatalytic nature, decreasing rapidly with the evolution of nitrogen until a composition close to that of Fe_3N is reached. The rate of decomposition of Fe_3N into Fe_4N is much slower than the initial Fe_2N rate, is many times faster than the decomposition of Fe_4N, and at several temperatures is nearly independent of the fraction of the sample decomposed.

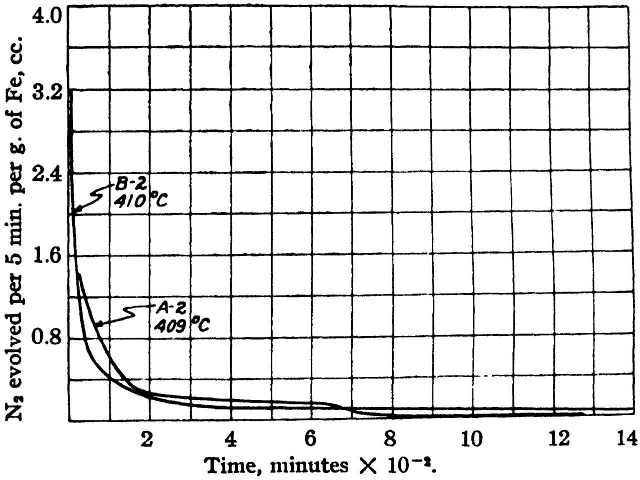

Fig. 3.—Rate of decomposition of Fe_2N into Fe_4N.

Reduction of the Iron Nitrides by Hydrogen

The Fe_2N samples prepared from the various catalysts reduce much more rapidly in hydrogen at about 180° than do the Fe_4N samples. Typical Fe_4N reduction curves, as shown in Fig. 4, indicate that the reaction is slightly if at all autocatalytic. A distinct maximum in the curve was always obtained about ten or fifteen minutes after the beginning of a two-hour reduction run; this apparent maximum might, however, be due to the adsorption of ammonia by the samples, since these were initially carefully flushed with nitrogen to zero ammonia content at the temperature of the run. The agreement between successive reduction runs is illustrated by runs 33 and 34 at 245°.

Two reduction curves for Fe_2N shown in Fig. 4 are characterized by unusually sharp maxima. x-Ray photographs of samples which during a similar run were removed before reaching the maximum reduction rate and at two successive points after reaching the maximum showed increasing amounts of Fe, decreasing amounts of Fe_2N and Fe_3N, and no Fe_4N. The photographs were not sufficiently clear to permit differentiation between Fe_2N and Fe_3N.

Discussion

Mittasch, Kuss and Emert[2] have studied the rate of ammonia decomposition over Fe_2N and compared it with the rate of nitrogen evolution from Fe_2N *in vacuo*. In the course of their work they measured the rate of nitrogen evolution from a sample of promoted iron synthetic ammonia catalyst that had been converted into Fe_2N. The decomposition curves for 350 and 400° published in Fig. 8 of their article permit one to estimate approximately the rates of decomposition of the Fe_4N portion of their nitrides at these two temperatures. The temperature coefficient calculated from the curves corresponds to about 45,000 calories energy of activation for the Fe_4N decomposition, which agrees satisfactorily with the average value, 50,000 calories, found in the present work. They point out that the Fe_2N decomposed at practically a constant rate until about one-half the nitrogen was evolved. Our own results showed similarly constant rates for Fe_3N and Fe_4N under favorable conditions but not for Fe_2N.

Winter[3] has recently studied the rate of ammonia decomposition over iron. In the course of his experiments he found that the energy of activation of the decomposition was about 50,000 calories per mole of ammonia. Furthermore, the kinetics he obtained indicated that the slow step in the reaction was the escape of nitrogen from the surface of the catalyst. It is interesting to note that the temperature coefficient of the decomposition of Fe_4N in our own experiments corresponded to an energy of activation of about this same value.

On several different occasions attempts have been made to correlate the rate of surface reactions with the frequency, f, with which the energy of a surface atom or molecule has an opportunity to readjust itself. Thus, for example, Topley[4] pointed out that if it be assumed that the molecules of adsorbed ammonia on tungsten or platinum have a chance to readjust their energies 10^{12} times per second, then from the known areas of metal involved it can be shown that the observed rate can be accounted for by assuming that the fraction $e^{-E/RT}$ of these energy changes will result in the adsorbed ammonia molecules picking up the observed energy of activation E. The value 10^{12} is about the magnitude of the "restrahlen" vibration frequencies for solids. In an analogous way it is interesting to show by calculation whether or not the observed rate of nitrogen evolution in the zero order decomposition of Fe_4N made from a doubly promoted catalyst can be accounted for by similar postulates. If every nitrogen atom (or molecule) on the surface of the Fe_4N sample gets a chance to change its energy content f times per second, and if all atoms (or molecules) picking up the 50,000 calories per mole average energy of activation noted in the present work escape from the surface, then the rate r of nitrogen evolution in cc./min./g. of iron will be given by the equation $nfe^{-E/RT}$ (60) = r, where n is the number of cc. of nitrogen constituting a monomolecular surface layer on 1 g. of iron, f is the atomic vibration frequency for Fe (about 10^{12} times per second), and E is the energy of activation observed in the present experiments for the thermal decomposition of Fe_4N. An approximate value for n obtainable from the poisoning experiments of Almquist and Black[5] and from some recent adsorption experiments of Emmett and Brunauer[6] is 1 cc. of nitrogen per gram of iron. Inserting 50,000 calories for E and 10^{12} for f, the calculated value of r is 0.17 cc. per minute per gram of iron at 430°. The experimental value is 0.06 cc. per gram. This agreement is of course much better than the accuracy with which the values of E or of n are known. It indicates however that the observed rate is of the right magnitude to be explained on such a basis.

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[2] Mittasch, Kuss and Emert, *Z. Elektrochem.*, **34**, 829 (1928).

[3] Winter, *Z. physik. Chem.*, **B13**, 401 (1931).

[4] Topley, *Nature*, **128**, 115 (1931).

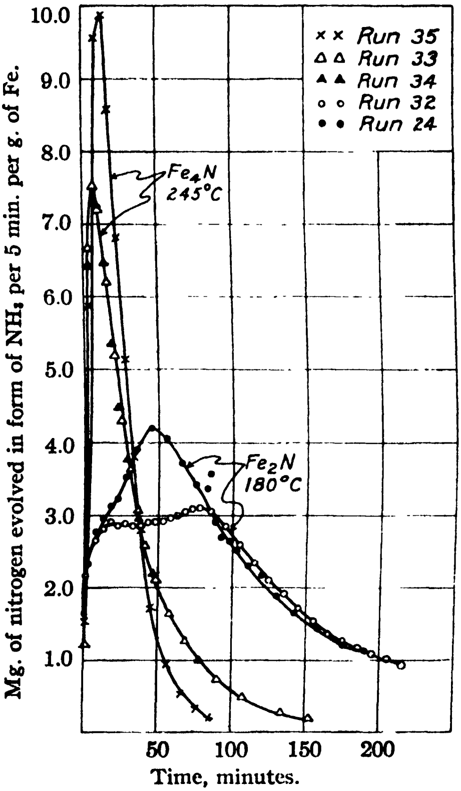

Fig. 4.—Rate of reduction of Fe_4N and Fe_2N by hydrogen.

Attention should be called to one other interesting experimental observation in connection with the thermal decomposition of Fe_4N made from a doubly promoted catalyst. In a decomposition experiment on sample B-3 shown in Fig. 1 and in three other similar experiments on Fe_4N samples from this same doubly promoted catalyst, an abrupt decrease in the rate

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(5) Almquist and Black, THIS JOURNAL, **48**, 2814 (1926).

(6) Emmett and Brunauer, *ibid.*, **55**, 1738 (1933).

of nitrogen evolution occurred at the end of the run. The volume of gas evolved after the beginning of this abrupt rate decrease was in all cases about that estimated to correspond to a monomolecular surface layer, being between 1 and 3 cc. of nitrogen per gram of iron. This is in accord with the hypothesis that the escape of nitrogen from the surface of the iron is the slowest step in the decomposition, the sudden break in the rate curve being naturally associated with the point at which all except the surface nitrogen has escaped. However, if the rate of diffusion of nitrogen through iron at 430° is sufficiently great, then the 1 to 3 cc. of nitrogen evolved after the break might include some of the dissolved nitrogen as well as nitrogen adsorbed on the surface of the iron.

The reduction curves for Fe_2N shown in Fig. 4 can be explained as a summation of two non-autocatalytic reactions: $3/2H_2 + 3Fe_2N = 2Fe_3N + NH_3$ and $3/2H_2 + Fe_3N = 3Fe + NH_3$. The very sharp maxima in the Fe_2N reduction curves seem more consistent with this interpretation than with the conclusion that the reduction of Fe_2N proceeds to Fe in one step and is autocatalytic.

In one experiment on the reduction of Fe_2N part of the experimental points were obtained by flushing out any adsorbed ammonia between each five-minute reduction period. These points and those obtained without such flushing lay equally well on the reduction curve, thus showing definitely that the adsorption of ammonia is not sufficiently large to account for the initially low ammonia values obtained at the start of each Fe_2N reduction run.

Summary

The rates of decomposition and of reduction by hydrogen of Fe_4N and Fe_2N made from active and from rather inactive iron synthetic ammonia catalysts have been determined. The decomposition of Fe_4N entails an energy of activation of about 50,000 calories. Fe_4N prepared from active catalysts decomposes more rapidly than that prepared from less active catalysts.

WASHINGTON, D. C.

RECEIVED JUNE 12, 1933
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

Densities of Mixtures of Benzene with Phenylethyl Alcohol and with Methyl Salicylate

BY RAYMOND C. GLOWASKI AND CECIL C. LYNCH, JR.

In a study of volume relations in mixtures of non-polar liquids it was observed that there were no data available on densities for two of the binary mixtures studied: namely, benzene–phenylethyl alcohol and benzene–methyl salicylate. The present investigation was undertaken to determine at 25° densities of these binary mixtures at various concentrations.

Materials.—Benzene C. P. and phenylethyl alcohol from the Eastman Kodak Company were allowed to stand over anhydrous calcium chloride for about a week and then fractionally distilled at 761 mm. The fraction of benzene boiling between 79.7 and 80.0° and that of phenylethyl alcohol boiling between 217–219° were collected and showed densities of 0.8724 and 1.0160, respectively, at 25°. Repeated distillations failed to alter the density. These densities agreed well with values obtained by Tyrer and by Washburn and Read,[1] for benzene, and by Szamatolski for phenylethyl alcohol.[2]

Methyl salicylate (artificial oil of wintergreen from Eimer and Amend), after the passage through it of dry air for several hours at its boiling point, was fractionally distilled at 18–19 mm. The definitive fraction was collected between 106.9 and 108.1° and showed a density of 1.080 at 25° in good agreement with the values given by Umney.[3]

Density Measurements.—The solutions were prepared by direct weighing of the components into tared glass-stoppered bottles, the more

TABLE I

DENSITIES OF BINARY MIXTURES AT 25°

Benzene–phenylethyl alcohol			Benzene–methyl salicylate		
Mol. frac. alcohol	% Alcohol by wt.	d_4^{25}	Mol. frac. ester	% Ester by wt.	d_4^{25}
0.0000	0.00	0.8724	0.0000	0.00	0.8724
.0931	13.83	.8898	.1016	18.06	.9136
.2000	28.11	.9096	.1800	29.96	.9434
.3066	40.89	.9277	.2907	44.40	.9838
.4125	52.34	.9437	.3947	55.95	1.0188
.5016	61.13	.9569	.5139	67.34	1.0551
.6068	70.71	.9705	.5980	74.34	1.0796
.7402	81.68	.9882	.7061	82.40	1.1089
.8202	87.71	.9972	.8136	89.48	1.1337
.9335	95.64	1.0092	1.0000	100.00	1.1798
1.0000	100.00	1.0160			

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[1] Tyrer, *J. Chem. Soc.*, **97**, 2620 (1910); Washburn and Read, THIS JOURNAL, **41**, 729 (1919).

[2] Szamatolski, *Ind. Eng. Chem.*, *News Ed.*, **11**, 114 (1933).

[3] Umney, *Perf. Essent. Oil Record*, **7**, 344 (1916), from *C. A.*, **11**, 866 (1917).

volatile benzene being added last. The samples were then well shaken and placed in a thermostat at 25.00 ± 0.05° for four to six hours. Pycnometers (of 5 or 25 cc. volume) which had been carefully standardized with distilled water were then filled with the mixtures and kept in the thermostat for two hours. The liquids were in all cases completely miscible.

The densities given in the table are all means of at least three determinations which never differed from one another by six units in the fourth decimal place. The average deviation of these measurements from the means for all the observations was one unit in the fourth decimal place.

Summary

Densities of mixtures of benzene and phenylethyl alcohol and of benzene and methyl salicylate have been determined over the entire range of concentration.

NEWARK, DELAWARE

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Induced Oxidation of Anthracene in the Autoxidation of Benzaldehyde

BY G. E. K. BRANCH, H. J. ALMQUIST AND E. C. GOLDSWORTHY

Introduction

It is well known that inhibition of the autoxidation of benzaldehyde by anthracene is temporary. When small quantities of anthracene are added to a benzaldehyde–oxygen mixture, there is a slow absorption of oxygen, which accelerates until the normal rate of absorption of oxygen by benzaldehyde is reached. At this stage the anthracene has been almost entirely oxidized to anthraquinone. This oxidation is an induced reaction, for it does not occur in an inert solvent.

The most likely mechanisms for oxidations of inhibitors are (1) that the inhibitor is oxidized by a link in the autoxidation chain, the products of this reaction being incapable of carrying on the chain, and (2) that the inhibitor is oxidized by the peroxide molecules that are dropped out of the autoxidation chain.

Alyea and Bäckström[1] have conclusively shown that in the inhibition of the autoxidation of sodium sulfite by several alcohols the breaking of the autoxidation chain and the induced oxidation are a single process. Bäckström and Beatty[2] have assumed the same to be true of the autoxidation of benzaldehyde inhibited by anthracene. The evidence was that measurements on extrapolation to high concentrations of anthracene showed a molal equivalence between the anthraquinone and benzoic acid formed. It was necessary for the authors to assume that the first product in the oxidation of anthracene absorbed oxygen to form anthraquinone without the assistance of the oxidation of benzaldehyde.

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(1) Alyea and Bäckström, THIS JOURNAL, **51**, 90 (1929).

(2) Bäckström and Beatty, *J. Phys. Chem.*, **35**, 2530 (1931).

Measurements of the rate of absorption of oxygen by benzaldehyde in the presence of varying quantities of anthracene can be used to prove the identity of the act of inhibition with the mechanism of the induced oxidation, and, if the proof is satisfactory, to obtain the rate of initiation, and average length of the chains, which are the fundamental constants of the autoxidation.

Oxidation Induced by Inhibition.—On the assumption that the breaking of a chain is always accompanied by the oxidation of a molecule of anthracene, and is the only source of this induced reaction, we may follow Alyea and Bäckström[1] and set up the equations,

$$\mathrm{d}O/\mathrm{d}t = k_0k_1/(k_2 + k_3A) \qquad (1)$$

and

$$-\mathrm{d}A/\mathrm{d}t = k_0k_3A/(k_2 + k_3A) \qquad (2)$$

in which O is the oxygen absorbed, k_0 is the rate of initiation of chains and $k_1/(k_2 + k_3A)$ is the average length of the chains in inhibited autoxidation. This last expression involves k_1, k_2, k_3 and A, which are the specific rate constants of the chain-continuing process, of the normal chain-breaking reaction and of the chain-breaking reaction involving anthracene and the concentration of anthracene, respectively.

Inspection of equation (2) shows that when k_3A is large with respect to k_2, $-\mathrm{d}A/\mathrm{d}t$ is independent of the concentration and kind of inhibitor. The measurements of Alyea and Bäckström show that this condition is fulfilled in the autoxidation of sodium sulfite inhibited by high concentrations of alcohols.

Combining equations (1) and (2) gives

$$-\mathrm{d}O/\mathrm{d}A = k_1/k_3A \qquad (3)$$

Integration of equations (2) and (3) gives

$$t = \frac{1}{k_0}\left(\frac{k_2}{k_3}\log\frac{A_0}{A} + A_0 - A\right) \qquad (4)$$

and

$$O = \frac{k_1}{k_3}\log\frac{A_0}{A} \qquad (5)$$

Hence

$$t = \frac{1}{k_0}\left\{\frac{k_2O}{k_1} + A_0(1 - e^{-k_3O/k_1})\right\} \qquad (6)$$

in which A_0 is the initial concentration of anthracene.

Figure 1 shows a series of plots of oxygen absorbed against time for autoxidations of benzaldehyde, inhibited by varying initial concentrations of anthracene. The shapes of these curves are those that would be expected from equation (6), if k_3 is large with respect to k_2. But equation (6) demands that the time taken to absorb a given quantity of oxygen be a linear function of the initial concentration of anthracene with the origin at the time taken in the absence of an inhibitor. This is not true when the concentration of benzoic acid is high.

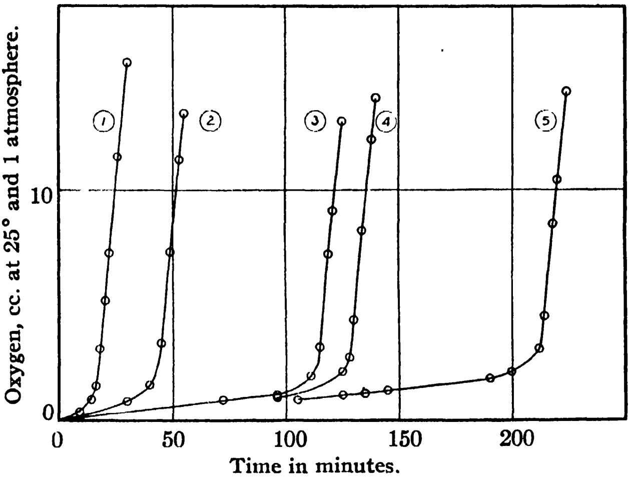

Fig. 1.—Oxygen absorption curves obtained with mixtures of benzaldehyde, benzoic acid, 0.444 molal, and anthracene at the following molalities: 1, 0.000040; 2, 0.000080; 3, 0.000132; 4, 0.000140; 5, 0.000200.

In Table I the times taken to absorb 5 cc. of oxygen at varying initial concentrations of anthracene and benzoic acid are shown. The numbers in the last column of this table are the times taken to absorb 5 cc. of oxygen

TABLE I

TIMES TAKEN TO ABSORB 5 CC. OF OXYGEN AT VARIOUS INITIAL CONCENTRATIONS OF ANTHRACENE AND BENZOIC ACID

Init. benzoic acid (moles/liter)	Time t, for abs. of 5 cc. of O_2, min.	A_0, init. anthracene (moles/liter)	$(t - 5)/A_0 \times 10^{-6}$	Init. benzoic acid (moles/liter)	Time t, for abs. of 5 cc. of O_2, min.	A_0, init. anthracene (moles/liter)	$(t - 5)/A_0 \times 10^{-6}$
0.444	5.0	0.0	...	0.087	5.0	0.0	...
	19.9	.000040	3.7		40.0	.000100	3.3
	46.6	.000080	5.2		112.4	.000244	4.1
	106.8	.000132	7.7		176.0	.000356	4.8
	130.6	.000140	9.0	.074	5.0	0.0	...
	214.0	.000200	10.5		69.0	.000200	3.2
.229	5.0	0.0	...		152.0	.000400	3.7
	47.0	.000090	4.6				
	72.2	.000124	5.4				
	146.0	.000200	7.1				

minus five minutes, the time that would be taken in the absence of any inhibitor, divided by the corresponding initial concentrations of anthracene. According to equation (6) this quantity should be a constant, whereas it increases with increasing initial concentrations of anthracene, this increase being most accentuated at the higher initial concentrations of benzoic acid.

There are other observations that militate against the theory that in the autoxidation of benzaldehyde inhibitors are oxidized only in the act of inhibition. It can be seen from Fig. 1 that the approach to a normal reaction after a period of inhibition is very rapid. The times taken to reach 90 and 95% of the normal rate of absorption of oxygen differ but little. It is therefore possible to measure fairly definitely the time taken to oxidize practically all of the inhibitor, and to obtain approximately an average rate for this reaction by dividing the initial concentration of the inhibitor by this time. But according to equation (4) these fairly definite inhibition periods could be obtained only if $k_2/k_3 \log A_0/A$ is small with respect to A_0, even when A is so small that the rate of absorption of oxygen is nearly that in the absence of inhibitor. The average rate of oxidation of the inhibitor will then be k_0, which is independent of what inhibitor is used. Also the presence of an extraneous substance that by itself has little inhibitory power should not affect this rate. These expectations are not fulfilled. Anthracene, phenanthrene, potassium iodide and hydroquinone are oxidized at very different rates. Benzoic acid, which by itself has only a small influence on the rate of absorption of oxygen by benzaldehyde, has a marked action on the rate of oxidation of some inhibitors. It decreases the rate of the induced oxidations of anthracene and of potassium iodide, increases that of hydroquinone, but does not affect that of phenanthrene. These facts are shown in Table II.

TABLE II

AVERAGE RATE OF OXIDATION OF SOME INHIBITORS IN MOLES PER LITER PER MINUTE, IN THE ABSENCE OF INITIAL BENZOIC ACID, AND WITH 0.073 *M* BENZOIC ACID

Inhibitor	Concentration, moles/liter	Av. rate without initial benzoic acid	Av. rate with initial benzoic acid
Anthracene	0.0002	0.00001	0.000003
Phenanthrene	.001	.0001	.0001
Potassium iodide	.00002	.0000003	.00000015
Hydroquinone	.0004	.00002	.00004

Induced Oxidation by Peroxides.—The alternative mechanism for the oxidation of inhibitors is a reaction between the inhibitor and peroxide molecules that have insufficient energy to carry on the chain. These peroxides are present in measurable quantities during autoxidations. In the case of the autoxidation of benzaldehyde inhibited by anthracene, the isolatable perbenzoic acid cannot be assigned the role of oxidizer of the inhibitor, for its action on anthracene is known to be too slow. However, it has been shown that peroxides more reactive than perbenzoic acid are present during the autoxidation of benzaldehyde. That anthracene is destroyed by these peroxides is easily demonstrable.

When the autoxidation of benzaldehyde is allowed to occur for a few minutes, the absorption of oxygen is inhibited on the addition of anthracene, but regains its normal rate in a much shorter time than it does when the same charge of anthracene is added before the admission of oxygen. Thus in a reaction started with 0.444 *M* benzoic acid and 0.0002 *M* anthracene, the normal rate of absorption was reached more than two hundred minutes after the start of the reaction, but when the same amount of anthracene was added after the reaction had proceeded for eleven minutes, the period of inhibition was only nineteen minutes. This experiment is depicted in Fig. 2. The curve shown in Fig. 2 should be compared with that on the extreme right in Fig. 1.

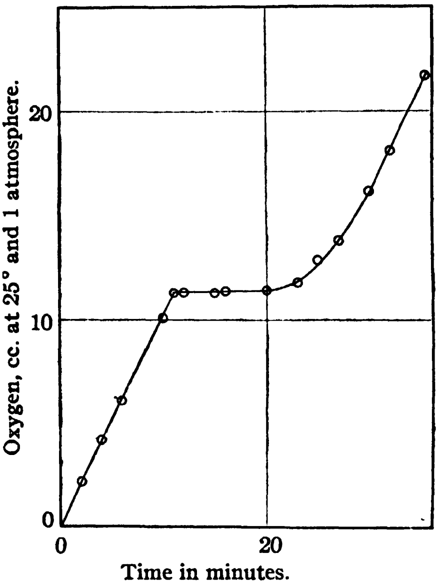

Fig. 2.—Oxygen absorption curve obtained by adding anthracene to a concentration of 0.0002 molal eleven minutes after the reaction of a mixture of benzaldehyde and benzoic acid 0.444 *M* had started.

In this experiment the anthracene is oxidized by peroxides whose concentrations are rapidly diminishing below the values of the steady state of normal reaction, for they are being used up by reaction with benzaldehyde. The way in which this occurs is pictured in Fig. 3, which shows an experiment in which the oxygen is removed by evacuation after an autoxidation has been started. The descending branch of curve 3 shows a removal of peroxides, which is approximately first order with respect to peroxides. The rate constant is about 0.13 reciprocal minutes.

Benzoic acid has a remarkable effect in increasing the life of anthracene exposed to an oxygen-benzaldehyde mixture. This can be described in terms of the times taken to achieve normal rates of absorption of oxygen,

Table III

Variation of Time Taken to Absorb 5 Cc. of Oxygen with Initial Concentration of Benzoic Acid

Initial concentration of anthracene = 0.0002 *M*

Initial concn. of C_6H_5COOH in mole/liter	0	0.039	0.074	0.100	0.229	0.444
Time taken to absorb 5 cc. of O_2 in minutes	20	55	70	105	145	214

or more definitely in terms of the times taken to absorb a chosen amount of oxygen.

This effect of benzoic acid can be explained by the theory of oxidation of the inhibitor by non-chain-continuing peroxide molecules. The oxidation of an inhibitor competes with that of benzaldehyde. It has been shown[3] that the oxidation of benzaldehyde is preceded by an interaction between peroxide and benzoic acid. If this interaction increases the relative chance of the oxidation of benzaldehyde over that of the inhibitor, benzoic acid prolongs the inhibition period, but if the reverse is true it diminishes the inhibition period. The former case is exemplified by anthracene and potassium iodide, the latter by hydroquinone. The oxidation of phenanthrene is not affected by benzoic acid, possibly because this very rapidly oxidized inhibitor attacks the peroxide even before the latter has time to react with benzoic acid.

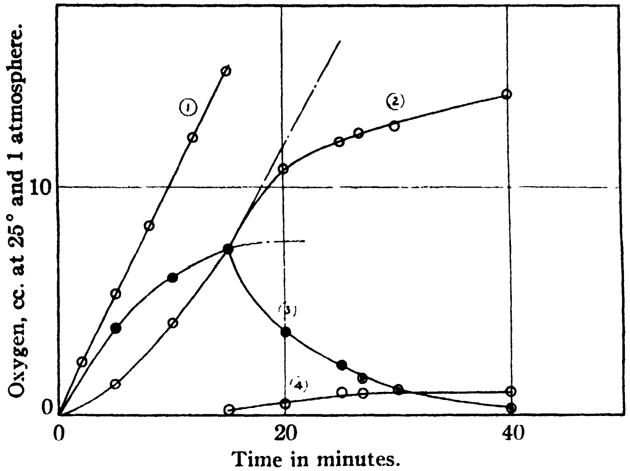

Fig. 3.—The variation with time of the distribution of absorbed oxygen in experiments started with a mixture of benzaldehyde and benzoic acid in which the oxygen was evacuated after fifteen minutes of reaction: 1, the total oxygen absorbed; 2, the oxygen as benzoic acid; 3, the oxygen as peroxides; 4, the oxygen discrepancy.

On the assumption that all of the anthracene is oxidized by peroxides incapable of continuing the autoxidation chain, the absorption of oxygen in the presence of anthracene can be expressed by the differential equations

$$\mathrm{d}O/\mathrm{d}t = k_0k_1/(k_2 + k_3A) \qquad (1)$$

$$-\mathrm{d}A/\mathrm{d}t = k_4PA, \text{ and} \qquad (7)$$

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{k_0k_1}{k_2 + k_3A} - f(P,A,B) \qquad (8)$$

in which P is the concentration of peroxides, and $f(P,A,B)$ is a function of peroxide, anthracene and benzoic acid concentrations, and represents the rate at which peroxides are used up.

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(3) Almquist and Branch, THIS JOURNAL, 54, 2293 (1933).

A rough test of equation (7) may be obtained by measurements of the peroxide concentrations and rates of absorption of oxygen during inhibition. Such measurements are shown in Fig. 4.

Equations (1) and (7) can be combined to give

$$\frac{d^2O}{dt^2}\Big/P\,\frac{dO}{dt}\left(1-\frac{k_2}{k_0k_1}\,\frac{dO}{dt}=k_4\right) \tag{9}$$

k_0k_1/k_2 is the normal rate of absorption of oxygen and is about one cc. per minute.

The approximate constancy of k_4 is shown in Table IV. The values given in this table are derived from the curves shown in Fig. 4.

Table IV

Peroxide Concentrations, Rates of Absorption of Oxygen and Acceleration of Rate of Absorption near the End of Inhibition Period

Initial anthracene = 0.000125 *M*. Initial benzoic acid = 0.444 *M*

Time, min.	Peroxide concentration, cc.	dO/dt, cc./min.	d^2O/dt^2, cc./min.^{2}	k_4
95	0.45	0.038	0.002	0.12
99	0.60	.051	.004	.14
103	0.83	.081	.010	.16
107	1.30	.15	.024	.15
110	1.95	.27	.057	.15
113	2.85	.52	.12	.17
114	3.17	.65	.13	.18
				Average 0.15

In Fig. 4 and Table IV we have used the equivalent of one cc. of oxygen as a concentration unit. Throughout all our experiments 2.25 cc. of benzaldehyde was used, and the oxygen was measured at 25° and one atmosphere. One cc. of oxygen corresponds to 0.0182 mole per liter. The rate constant, k_4, is therefore about 8.2 in the more usual units liters per mole per minute.

Inspection of Fig. 4 shows that an amount of benzoic acid equivalent to 1 cc. of oxygen, that is, 0.0182 *M*, is formed before the anthracene is all used up. The initial anthracene was 0.000125 *M*. It is therefore apparent that nearly all of the peroxide formed is eventually reduced by benzaldehyde rather than by anthracene. As a large quantity of benzoic acid was present at the start (0.444 *M*), the main reduction of the peroxides occurs at a constant rate, and the function ($f(P,A,B)$ of equation (8) is proportional to *P*. Although this simplification is insufficient to permit the expression of oxygen absorbed in terms of the time and the initial concentration of anthracene, it is obvious that the solution of equations (1), (7) and (8), with the above simplifications will give the time to absorb a chosen volume of oxygen as approximately a linear function of the initial concentration of anthracene. This follows, because in by far the greater part of the inhibition period, dP/dt is very small. But as has already been mentioned this time is a higher order function of the initial concentration of anthracene. Further we have observed that this phenomenon is more marked with high than with low concentrations of benzoic acid. Both of these observations are shown in Table I.

The most natural resolution of this paradox is that the peroxide is not a single substance, but is a mixture of small quantities of more active with larger quantities of less active peroxides. A large fraction of the more active peroxides is reduced by anthracene. Their concentration is a quadratic function of the reciprocal of the concentration of anthracene, for they are formed more slowly and are used up more rapidly at high than at low concentrations of anthracene. Hence $-dA/dt$ is a decreasing function of A, and the time taken to absorb 5 cc. of oxygen increases more than proportionally with increase in the concentration of anthracene.

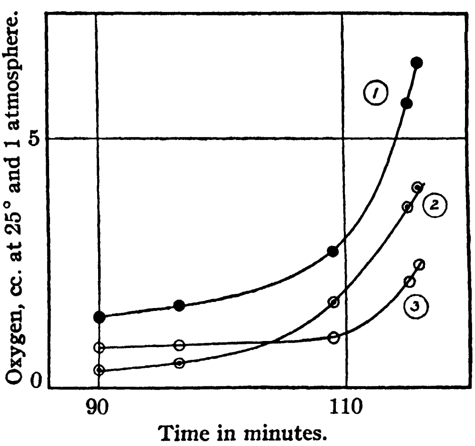

Fig. 4.—The variation with time of the distribution of absorbed oxygen during an induction period: 1, the total oxygen absorbed; 2, the oxygen as peroxides; 3, the oxygen as benzoic acid.

That this phenomenon is more marked with high than with low concentrations of benzoic acid indicates that the rate of oxidation of anthracene relative to that of combination with benzoic acid is greater for the more active than for the less active peroxides. When the concentration of benzoic acid is low, most of the induced reaction occurs through the less effective but more abundant peroxides, and the rate of oxidation of anthracene is approximately independent of its concentration. But when the concentration of benzoic acid is high a greater fraction of the induced reaction is carried by the more effective peroxides, and the decrease in the rate of oxidation of anthracene with increase in its concentration is marked.

Bäckström and Beatty's[2] evidence of an equivalence between anthracene oxidized and benzoic acid formed at high concentrations of anthracene shows that anthracene not only is oxidized by peroxide molecules of insufficient energy to propagate the autoxidation chain, but also is oxidized by peroxide molecules that are links in this chain. It must therefore be assumed that anthracene is oxidized (1) in the act of inhibition, (2) by non-chain-continuing peroxides that react with anthracene in preference to benzoic acid and (3) by similar peroxides that react with benzoic acid in preference to anthracene. At very high concentrations of anthracene, non-chain continuing peroxides are rare and the first mechanism predominates. At low concentrations of anthracene the other two mechanisms predominate, their relative effectiveness being largely determined by the concentration of benzoic acid. This theory of the combined action of chain-continuing and non-chain-continuing peroxides has been sponsored by Stephens[4] for the induced oxidation of inhibitors in general.

Experimental Part

In these experiments the benzaldehyde and benzoic acid must be very pure. The benzaldehyde was purified by repeated fractional distillations in an atmosphere of carbon dioxide and was kept in the dark under an excess pressure of this gas. The benzoic acid was purified by repeated crystallizations from water. The standards of purity were the absence of all signs of an induction period in the absence of deliberately added inhibitors, and the ability to obtain within ten per cent. of the normal rate of absorption of oxygen at the end of an inhibition period produced by an inhibitor. The anthracene and other inhibitors were ordinary C. P. chemicals. They were added immediately before an experiment, for, even with the greatest care, it was found that solutions of anthracene in benzaldehyde lost some anthracene when kept.

The reactions were all carried out in the dark, in the same vessel and with uniform shaking. The change in the volume of oxygen was measured

TABLE V

DATA FOR THE CURVES SHOWN IN FIGURE 1

Initial concentration of benzoic acid = 0.444 *M*

	Time, minutes	O_2 absorbed, cc.	Time, minutes	O_2 absorbed, cc.	Time, minutes	O_2 absorbed, cc.
A_0 = 0.00004 *M*	9	0.4	18	3.1	26	11.4
	14	0.9	20	5.2	30	15.5
	16	1.5	22	7.3		
A_0 = 0.00008 *M*	30	0.8	45	3.4	53	11.2
	40	1.5	49	7.3	55	13.3
A_0 = 0.000132 *M*	72	0.8	115	3.2	121	9.1
	96	1.1	119	7.2	125	13.0
	111	1.9				
A_0 = 0.00014 *M*	96	1.0	130	4.3	138	12.2
	125	2.1	134	8.2	140	14.0
	128	2.7				
A_0 = 0.0002 *M*	105	0.9	190	1.8	218	8.5
	125	1.1	200	2.1	220	10.4
	135	1.2	212	3.1	224	14.3
	145	1.3	214	4.5		

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(4) Stephens, *Ind. Eng. Chem.*, **24**, 918 (1932).

in a constant pressure gas buret connected to the reaction vessel. Reaction vessel and gas buret were thermostated at 25°.

Peroxide and benzoic acid concentrations were measured by stopping the reaction and analyzing for peroxides with potassium iodide and sodium thiosulfate, and for benzoic acid by acidimetry. Curves in which the concentrations of these substances are shown are compounded from a series of experiments stopped at different times. A curve for the absorption of oxygen can be obtained in a single experiment.

The purification of materials, the apparatus, the methods of carrying out

TABLE VI

DATA FOR THE CURVE SHOWN IN FIGURE 2

Initial benzoic acid = 0.444 *M*

Time, minutes	O_2 absorbed, cc.	Time, minutes	O_2 absorbed, cc.	Time, minutes	O_2 absorbed, cc.
2	2.2	6	6.1	11	11.3
4	4.2	10	10.1		
Anthracene added to give 0.0002 *M* solution					
12	11.3	23	11.8	30	16.2
15	11.3	25	12.8	32	18.1
16	11.4	27	13.8	35.4	21.7
20	11.4				

TABLE VII

DATA FOR THE CURVES SHOWN IN FIGURE 3

Time, minutes	O_2 absorbed, cc.	Peroxide, cc. of O_2	Benzoic acid formed, cc. of O_2	Rate constant for reduction of peroxides by benzaldehyde (reciprocal minutes)
2	2.3	..	..	..
5	5.2	3.7	1.3	..
8	8.2	..	..	..
10	..	6.0	4.0	..
12	12.2	..	..	..
15	15.1	7.2	7.3	..
Oxygen evacuated				
20	..	3.65	10.7	0.136
25	..	2.1	12.0	.123
26.8	..	1.6	12.4	.128
30	..	1.1	12.7	.125
40	..	0.3	14.0	.127
				Av. = 0.128[5]

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(5) The rate of reduction of peroxides by benzaldehyde was found to vary somewhat in different preparations of benzaldehyde. The rate constant 0.13 reciprocal minutes given in Table VII checks that (0.14) obtained by dividing dO/dt (1 cc. per minute) by the steady state concentration of peroxides (7.2 cc.). In another preparation of benzaldehyde Almquist and Branch[6] obtained 0.18 reciprocal minutes by dividing the rate of formation of benzoic acid by the peroxide concentration, and in the same experiment dO/dt divided by the steady-state concentration of peroxides was 0.17 reciprocal minutes. Apparently the reaction is affected by traces of impurities, probably water or metallic salts. Its rate is quadrupled by 0.002 *M* $FeCl_3$.

Table VIII

Data for the Curve Shown in Figure 4

Initial benzoic acid = 0.444 *M*; initial anthracene = 0.000125 *M*

Time, minutes	O_2 absorbed, cc.	Peroxide, cc. of O_2	Benzoic acid formed, cc. of O_2
90	1.4	0.35	0.80
96.5	1.6	0.50	0.85
109	2.7	1.7	1.0
115.2	5.7	3.6	2.1
116	6.5	4.0	2.45

experiments and analyses need not be described in greater detail here, for a fuller account of them can be found in the earlier paper by Almquist and Branch.[3]

The experimental results from which the curves in Figs. 1, 2, 3 and 4 are shown in the appended Tables V, VI, VII and VIII. The additional results shown in Tables I, II and III are obtained from experimental results so similar to those shown in Table V that they need not be described in detail.

Summary

Measurements of the absorption of oxygen by benzaldehyde in the presence of benzoic acid and small concentrations of anthracene and some other inhibitors were made.

It is pointed out that the results obtained are not in agreement with the theory that the induced oxidation of anthracene in benzaldehyde occurs only in the act of inhibition.

It is shown by direct experiment that anthracene is oxidized by peroxides formed during the autoxidation of benzaldehyde. The rate of this reaction is first order with respect to each of the reactants. The rate constant has been measured.

The effect of benzoic acid on the induced oxidations has been explained on the basis of competitive reductions of the peroxides by the inhibitor and by benzaldehyde with preliminary combination with benzoic acid.

In order to explain the way in which the absorption of oxygen depends on the initial concentrations of anthracene and benzoic acid, it has been assumed that the peroxides responsible for the induced oxidation of anthracene are a mixture of substances or states having different specific reactivities toward anthracene, benzoic acid and benzaldehyde.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Heat Capacities of Cis and Trans Dichloroethylenes

BY A. R. OLSON AND F. W. BRITTAIN

In an investigation of *cis-trans* reactions which is in progress in this Laboratory, the heat capacities of the two forms of gaseous dichloroethylene were needed. No data for these substances were found in the literature, and so we determined them by the velocity of sound method. Eucken and Mücke[1] and Kneser[2] have discussed objections to the use of high frequency sound waves for heat capacity determinations. As will be seen later, these objections, apparently, do not apply to the dichloroethylenes in the temperature range in which we worked.

Briefly the method consists in determining the wave length of sound waves in the gas to be investigated. These waves are produced by a quartz crystal which is responding to an alternating current of known frequency. For an ideal gas the equation connecting heat capacity with the velocity of sound, W, is

$$C_v = \frac{R}{(MW^2/RT) - 1} = \frac{R}{\gamma - 1} \qquad (1)$$

For a gas obeying van der Waals equation we can write

$$C_v = R/(\gamma - 1 + \phi) \qquad (2)$$

in which

$$\phi = \frac{2aP}{(RT)^2} - \gamma\frac{2bP}{RT} \qquad (3)$$

if we neglect higher order terms. Since the correction due to first order terms is small, this procedure is justified.

The van der Waals constants a and b have not been determined, and so they were estimated by two different methods. In the first method the average effect of substituting a chlorine for a hydrogen was determined for six substances for which the a's and b's were known, and then twice this correction was made in the constant for ethylene. In the second method, the average percentage change in the constants due to replacing two hydrogens bound to carbon by a carbon–carbon double bond was determined for five substances, and this reduction was made in the constants for ethylene dichloride. By the first method $a = 0.0319$ and $b = 0.00455$ and by the second method $a = 0.0303$ and $b = 0.00437$. The average values, $a = 0.031$ and $b = 0.0045$ are probably accurate to about 10%. This uncertainty in a and b corresponds to an uncertainty of 0.05 calorie/deg. in the heat capacity and this is less than the average experimental error.

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(1) A. Eucken and O. Mücke, *Z. physik. Chem.*, **18B**, 167 (1932).

(2) Kneser, *Ann. Physik*, **11**, 777 (1931). Also by personal communication of as yet unreported results.

Apparatus.—Electrical circuits for sonic interferometers have been described so often in the literature[3] that the description of the circuit is here limited to the wiring diagram in Fig. 1. The variation of the current through the microammeter due to sonic interference was from 20 to 100 microamperes, depending on the distance separating the reflector from the crystal.

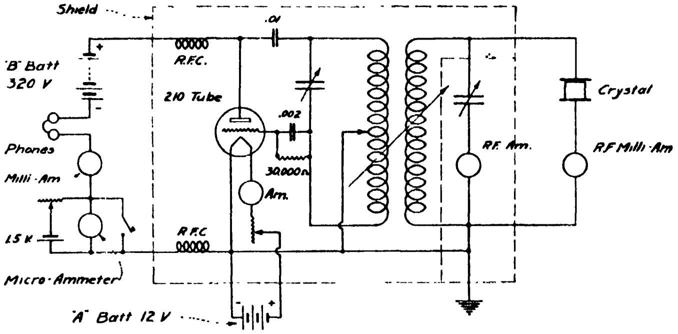

Fig. 1.—Wiring diagram for the sonic interferometer.

The quartz crystal was 28 × 23 × 22 mm. It was cut so that the 28 mm. axis was inclined about 18.5° away from the optic axis toward the mechanical axis, so as to get a vibration perpendicular to the face which was parallel to the reflector, as shown by Wright and Stuart.[4] The vibration frequency of the crystal was determined at various pressures and temperatures, not only directly by a General Radio standard wave meter, but also by checking by harmonic bracketing against several local broadcasting stations. The error in the frequency is estimated to be not more than 0.1%.

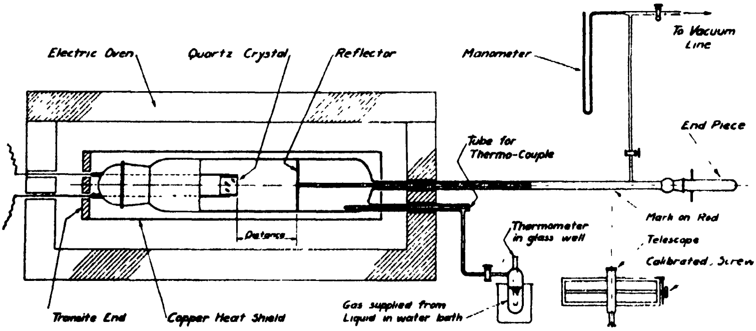

Fig. 2.—Assembly for measuring the velocity of sound.

The glass cylinder shown in Fig. 2 is about 70 mm. by 350 mm. The crystal mounting is depicted in Fig. 3. The reflector could be moved parallel to itself by turning the end piece. Positions of the reflector were read to 0.01 mm. The lubricant recommended by Meloche and Fredrick[5] was used on the joints exposed to the dichloroethylene. The gas pressure was determined by the temperature of liquid dichloroethylene

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(3) See G. W. Pierce, *Am. Acad. Arts Sci.*, **60**, 271 (1925); C. D. Reid, *Phys. Rev.*, **35**, 814 (1930).

(4) R. B. Wright and D. M. Stuart, *Bureau Standards Research Paper*, No. 356 (1931).

(5) C. C. Meloche and W. G. Fredrick, This Journal, **54**, 3264 (1932).

in the side-tube. The temperature of the gas in the cylinder was measured by a thermocouple. The temperature measurements are probably accurate to about 0.25°.

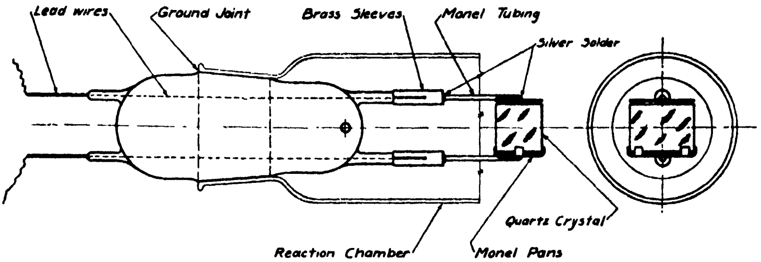

Fig. 3.—Mounting for quartz crystal.

The temperature of the gas between the oscillating crystal and the reflector was higher than the ambient gas due to the energy in the sound waves. This was checked not only by experiments on air at atmospheric pressure where all the data for computing the temperature from $w^2 = RT/M\ (C_p/C_v)$ are known, but also by inserting an alcohol thermometer in the path of the sound waves. For the crystal we used, a current through the crystal of 3.3 m. a. produced an increase of 0.3 degree in air at atmospheric pressure. By keeping the gas pressure and the current low enough, we were able to make this temperature correction unimportant.

Experimental Procedure

A new sample of gas was introduced into the reaction chamber for each run. The chamber was pumped out and filled with gas several times to eliminate air. The final pumping was run several hours at a pressure less than 10^{-3} mm. The pressure of the gas was taken as that corresponding to the temperature of the liquid and checked by the manometer. For the runs with the oven at room temperature the liquid was about

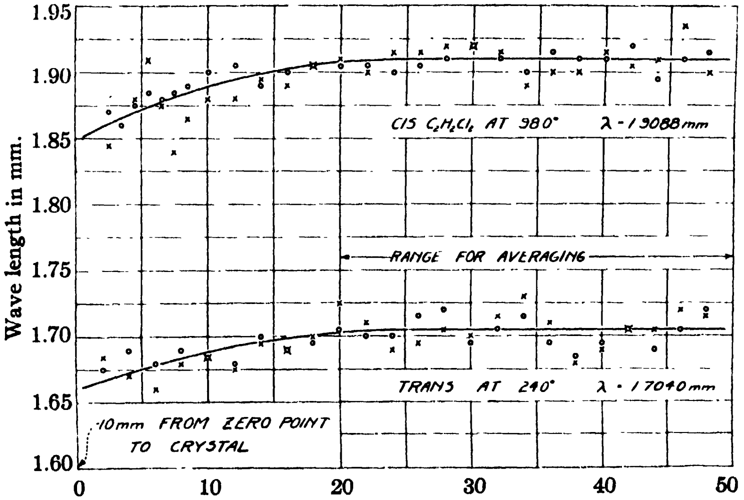

Fig. 4.—Typical curves of wave length as a function of the number of half waves separating the reflector from the crystal.

10° for the *cis* and at 0° for the *trans*. For runs at higher temperature the liquid was at room temperature for the *cis* and 8 to 10° for the *trans*. The oven, meanwhile, was heated to near the desired temperature and was allowed to stand for at least one hour to come to temperature equilibrium. The gas was allowed to stand in the reaction chamber with the crystal oscillating for at least half an hour before the run to ensure steady operation. For the runs, the reflector was set either 1 or 3 cm. away from the crystal and the first peak called the 0 or 20 half-wave position to correspond. The reflector was moved out and readings of distance taken for every other peak to the fiftieth peak and then repeated as the reflector was moved toward the crystal. The manometer, thermometers and other instruments were read before, at the middle and at the end of each run.

Typical readings of the wave length as a function of the number of half-wave lengths separating the reflector from the crystal are shown in Fig. 4. Due to the obvious trend in the wave length at small distances, only the sixteen readings between the twentieth and the fiftieth nodes were used for averaging. The average wave length was computed from $[(A + B \ldots N) - (a + b + \ldots n)]/N^2$ where $A, B \ldots N$ are the first eight readings and $a, b \ldots n$ are the second series of eight readings. From the two separate averages obtained as the reflector was moved in or out, a final average reading was computed for the runs. These final average wave lengths agreed within 0.1%.

Table I

Summary of Runs of *Cis* Dichloroethylene

Temp., °C.	Press., mm. Hg, p	Wave length, λ	Freq. kcy., f	Vel. sound, W	$\gamma = MW^2/RT$	C_v ideal gas[a]	Corr. term, ϕb[b]	C_v actual gas[b]
22.1	112	1.6965	100.80	171.00	1.1549	12.82	0.0064	12.31
71.9	161	1.8427	100.70	185.60	1.1641	12.11	.0065	11.64
97.7	168	1.9089	100.65	192.11	1.1605	12.38	.00575	12.02
98.1	168	1.9088	100.65	192.08	1.1589	12.50	.00575	12.06
140.2	181	2.0141	100.45	202.32	1.1547	12.84	.0048	12.46
162.3	180	2.0697	100.35	207.70	1.1576	12.60	.00450	12.25
163.7	180	2.0834	100.35	209.07	1.1667	11.91	.00450	11.60
192.9	173	2.1455	100.15	214.91	1.1556	12.76	.00345	12.58
240.5	180	2.2697	99.95	226.86	1.1713	11.80	.00300	11.60

[a] See Equation (1). [b] See Equations (2) and (3).

Table II

Summary of Runs of *Trans* Dichloroethylene

Temp., °C.	Press., mm. Hg., p	Wave length, λ	Freq. kcy., f	Vel. sound, W	$\gamma = MW^2/RT$	C_v ideal gas[a]	Corr. term, ϕb[b]	C_v actual gas[b]
24.0	124	1.7040	100.80	171.76	1.1578	12.59	0.0070	12.05
54.9	180	1.7861	100.75	179.95	1.1511	13.15	.0082	12.48
79.2	182	1.8577	100.70	187.07	1.1582	12.56	.0070	12.02
123.8	180	1.9763	100.70	198.70	1.1598	12.43	.0053	12.03
150.5	178	2.0395	100.40	204.77	1.1541	12.89	.0045	12.52
181.2	193	2.1149	100.25	211.98	1.1532	12.97	.0041	12.62
197.4	179	2.1607	100.15	216.39	1.1604	12.38	.0035	12.12
243.7	171	2.2735	99.90	227.12	1.1638	12.13	.0027	11.92

[a,b] See footnotes for Table I.

Results and Conclusions

The data and the computed values of C_v are summarized in Tables I and II and are shown on curves on Figs. 5 and 6. It is interesting to note the decrease of 1 to 2% in the wave length close to the crystal which occurred consistently in all tests whereas Pierce and Reid[3] working with air and carbon dioxide found an increase.

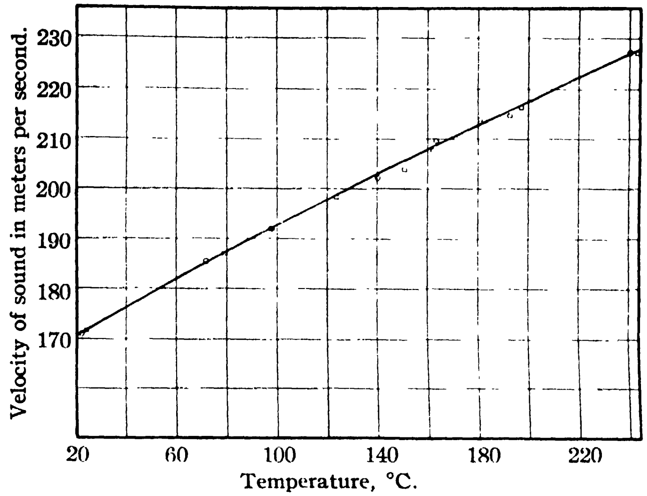

Fig. 5.—Velocity of sound in *cis*- and *trans*-dichlorethylene: ○; *cis*-dichloroethylene; □, *trans*-dichlorethylene.

The accuracy of the final results suffers from the nature of the equation, for the errors in measuring the velocity of sound are increased some fifteen times in computing C_v due to the fact that the velocity is squared and that γ (about 1.16) is so nearly equal to 1. Frequency and wave length were each measured to about 0.1%. This corresponds to an error of about 0.25 calorie in the heat capacity, agreeing with an average deviation of about 0.26 calorie for the individual experimental values.

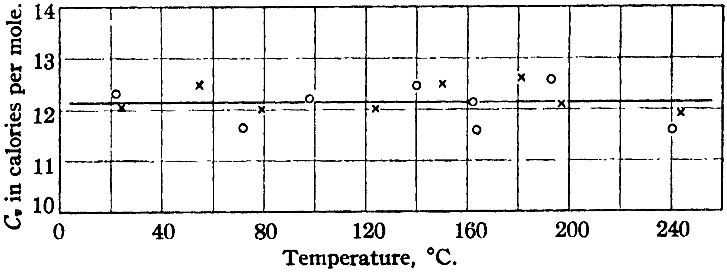

Fig. 6.—Heat capacity of *cis*- and *trans*-dichloroethylene: ○, *cis*-dichloroethylene; ×, *trans*-dichloroethylene.

Referring to Fig. 6, the data may be interpreted by assuming that C_v is the same for both gases and is constant over the whole range of temperatures with an average value of 12.14 ± 0.26 calories per mole.

Eucken and Mücke point out that with too high a frequency, the velocity of sound experiments on air and similar gases measures only a part of the vibrational energy. Kneser states that following a small and sudden change of pressure, each of the internal degrees of freedom, rotational and vibrational, requires a certain length of time to establish equilibrium with the translational degrees and that this time interval is a function of $h\nu/RT$. For a given temperature there is a critical frequency (or range of frequencies) below which the half period is relatively large and the particular internal degree is measured and above which the half period is too small for the degree to respond. For a given frequency and temperature, the internal degrees of freedom with relatively low $h\nu$ values will be measured and those with a relatively high $h\nu$ value will fail to respond. Due to the constancy of C_v over such a large temperature range, it appears to be quite likely that both forms of dichloroethylene have three vibration degrees of freedom of such low frequencies that they respond fully, and that the other nine vibrations have such high frequencies that they do not contribute appreciably to the heat capacity below 250°.

Acknowledgment is made to Mr. N. W. Garden, who constructed part of the apparatus, and to Mr. W. Maroney, who prepared the pure samples.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 377]

The Activity Coefficients of Hydrochloric Acid in Aqueous Solutions Containing Either Sodium or Potassium Perchlorate

BY STUART J. BATES AND JOSEPH W. URMSTON

Recent investigations,[1] both theoretical and experimental, have emphasized the fact that except in very dilute solutions, activity coefficients of strong electrolytes cannot be accurately calculated from theoretical considerations alone.

The original Debye–Hückel development of the ion attraction theory showed that in dilute solution the activity coefficient is chiefly determined by the ionic strength. Its dependence upon other factors was later taken into account and more accurate formulas derived. These involve constants whose numerical values must be determined from the data themselves.[1d] One of these constants "A" is related to the ionic diameters. By making certain assumptions regarding its value in mixtures of electrolytes, relatively simple relations between activity coefficients have been obtained.[2] The question as to the validity of such assumptions and relations must be settled by experiment.

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[1] (a) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); (b) Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924); (c) Noyes, *ibid.*, **46**, 1080, 1098 (1924); (d) Hückel, *Physik. Z.*, **26**, 93 (1925).

Of the electrolytes which have been investigated at various activities, hydrochloric acid has been the most carefully and extensively studied, both in its own pure solutions and in mixtures. However, previous investigators[3] of mixtures have restricted themselves to adding salts containing the chloride ion. In this paper, and in that by Murdoch and Barton which immediately follows, the effects of other types of electrolytes, including those which contain no ion in common with those of hydrochloric acid, are described.

The activity of hydrochloric acid and hence the mean activity of its ion in salt mixtures may be computed from measurements of the electromotive forces of cells of the type

$$H_2\ (1\ \text{atm.}),\ HCl\ (m_1) + \text{salt}\ (m_2),\ AgCl + Ag$$

The quantities concerned are related by the equation

$$E - E_0 = -(2RT/F)\ \ln m_1\alpha \qquad (1)$$

Here E is the measured electromotive force, E_0 the molal electrode potential, α the geometric mean activity coefficient of the ions of hydrochloric acid (more briefly, the activity coefficient of hydrochloric acid).

An added salt other than a chloride to be suitable for experiments of this nature must not react with the constituents of the cell and must possess certain other properties. Thus (1) it should be the salt of a strong acid, (2) the silver salt of its acidic constituent should be soluble, (3) it should not be the salt of an acid, like nitric acid, which may act as an oxidizing agent in solution and (4) it should be quite soluble. These conditions greatly restrict the choice of salts. However, sodium perchlorate appears to fulfil them admirably. Hence this salt was employed. In addition, in order to compare the relative effects of potassium and sodium ions, measurements were made employing potassium perchlorate; this salt is satisfactory except that it is not as soluble as could be desired.

Experimental Procedure

The cells used consisted of three silver–silver chloride half cells and two hydrogen half cells, each of the latter containing two hydrogen electrodes. The half cells were connected through stopcocks.

The hydrogen electrodes were of platinum foil, first covered electrolytically with a thin coating of gold and then with one of platinum black. They were washed with nitric acid and then with many changes of water; they were kept in water until placed in the cell. The hydrogen electrodes prepared in this manner checked to 0.02 or 0.03 millivolt.

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[2] Harned, THIS JOURNAL, **48**, 326 (1926).

[3] (a) Harned, *ibid.*, **38**, 1986 (1916); (b) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); (c) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1927); (d) Randall and Breckenridge, THIS JOURNAL, **49**, 1435 (1927).

Electrolytic silver and precipitated silver chloride prepared from dilute solutions according to the directions of Randall and Young[4] were used for the silver–silver chloride electrode. These electrodes checked one another to 0.1–0.2 mv. The final results for the cells at various concentrations showed an average deviation from the smooth curve of not more than 0.15 mv.

The cells were in an oil thermostat regulated to 25 ± 0.05°. The electromotive forces were measured by the aid of a type K Leeds and Northrup potentiometer using as a standard a Weston cell that was frequently checked against a cell recently certified by the Bureau of Standards.

The hydrochloric acid was obtained by diluting a c. p. acid to a density of 1.1 and distilling in an all-glass still, which had been repeatedly employed for this acid distillation. Only the middle portion of the distillate was used; it was diluted to the desired concentrations, and these were checked by the silver chloride gravimetric method. The sodium perchlorate was prepared by the addition of perchloric acid of c. p. grade to a c. p. sodium carbonate, the product was twice recrystallized from water. Potassium perchlorate (c. p.) was purified by three crystallizations from water. Conductivity water was used in the preparation of all solutions.

Several series of measurements were made. In each series the electromotive force of the cell containing a solution of hydrochloric acid only was first determined. Then to weighed quantities of this solution were added weighed amounts of the pure dry salt and the electromotive forces of the cells containing these solutions were measured. In this manner any uncertainty due to errors of a constant nature may be minimized.

TABLE I

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SOLUTIONS OF CONSTANT ACID CONCENTRATION BUT VARYING SODIUM PERCHLORATE OR POTASSIUM PERCHLORATE CONCENTRATION

$NaClO_4$ molality	E. m. f.	Activity coefficient
	HCl 0.2480 *M*	
0.0	0.3078	0.760
.1450	.3086	.749
.2428	.3089	.744
.2459	.3088	.745
.5484	.3079	.759
.7208	.3070	.772
	HCl 0.1015 *M*	
0.0	0.3513	0.795
.0887	.3537	.761
.1684	.3543	.750
.3069	.3548	.743
.5059	.3548	.743
.6985	.3542	.752
.8567	.3534	.765
.8902	.3532	.768
	HCl 0.04639 *M*	
0.0	0.3899	0.833
.01357	.3907	.820
.03989	.3920	.798
.0643	.3931	.783
.0987	.3938	.771
.1241	.3944	.763
.2150	.3953	.750
.2625	.3957	.745
.2633	.3956	.744
.2771	.3957	.745
.3722	.3959	.741
.4446	.3961	.739
.4635	.3961	.739
.6230	.3955	.747
.8460	.3946	.760
$KClO_4$ molality	E. m. f. HCl 0.0994 *M*	
0.0	0.3522	0.796
.00714	.3524	.793
.01318	.3529	.785
.01720	.3532	.780
.02476	.3533	.779
.05864	.3541	.767
.0884	.3548	.756
.0981	.3550	.754
.1219	.3554	.748

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(4) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

The experimental results are given in Table I. All concentrations are expressed as moles per 1000 g. of water.

The effect of added salt upon the activity coefficient of hydrochloric acid may be readily computed for each series of experiments from the relation

$$\ln \alpha/\alpha_0 = (F/2RT)\Delta E \qquad (2)$$

Here ΔE is the difference between the electromotive force of the cell containing hydrochloric acid at the concentration m_1 and that of the cell containing hydrochloric acid at the concentration m_1 and in addition an added salt; α_0 is the activity coefficient of the acid in the former solution, α its coefficient in the mixture.

Randall and Young[4] have made a careful study of all available data from which the activity coefficients of hydrochloric acid in its own pure solutions may be computed and have given a set of consistent values for 25°. We have taken our values for the pure solutions (α_0) from their results and have then computed values for mixtures by means of the above equation. Such values interpolated to round values of the acid concentration and of ionic strength are given in Table II.

TABLE II

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SODIUM PERCHLORATE AND POTASSIUM PERCHLORATE MIXTURES OF CONSTANT IONIC STRENGTH

Ionic strength	Pure HCl	HCl (m) + $NaClO_4$ $m = 0.25$	$m = 0.10$	$m = 0.05$	Ionic strength	Pure HCl	HCl (0.1 m) + $KClO_4$ $m = 0.10$
0.1	0.796	..	0.796	0.791	0.1	0.796	0.796
.25	.759	0.759	.754	.751	.15	.777	.769
.5	.757	.746	.742	.739	.20	.766	.754
.7	.773	.753	.749	.747			
1.0	.810	.776	.770	.767			

Discussion

These results will be considered here chiefly with reference to a relation which may be[2] obtained from the ion attraction theory with the aid of the assumption that the ionic diameters of all ions present in the solution are the same. This relation [see also Brönsted, THIS JOURNAL, **45**, 2898 (1923)] which applies to solutions of constant ionic strength is as follows

$$\log \alpha = \log \alpha_0 + k(\mu - m) \qquad (3)$$

Here α and m are the activity coefficient and molal concentration, respectively, of an electrolyte in a mixture of ionic strength μ; α_0 is its activity coefficient in its own pure solution of ionic strength μ; and k is a constant characteristic of both electrolytes.

Heretofore this relation has been tested only with salts containing the common chloride ion. Harned[3a] found this relation to hold closely for hydrochloric acid in the presence of added potassium, sodium or lithium chlorides at ionic strengths of 0.1, 1.0 and 3.0 molal; Hawkins[5] has shown

[5] Hawkins, THIS JOURNAL, **54**, 4480 (1932).

that the range for these three added chlorides extends to 6 molal. It holds less closely for sodium and potassium hydroxides in their corresponding chloride solutions at high ionic strengths.[6] Güntelberg[3b] determined the activity coefficients of hydrogen chloride in solutions of added lithium, sodium, potassium and cesium chlorides at an ionic strength of 0.1 molal. His results agree very closely with the requirements of the above equation.

In Fig. 1 are plotted for the ionic strengths 0.1, 0.25, 0.5, 0.7 and 1.0 the logarithms of the activity coefficients of hydrochloric acid in sodium perchlorate mixtures against concentrations *m* of the acid. The relations are linear, thus satisfying the requirements of equation (3). All of the lines have the same slope, namely, $k = 0.0244$. None of the points deviate from the linear relation by an amount corresponding to as much as 0.20 mv. In the same figure are plotted the corresponding values which Harned[2] obtained in this range of ionic strengths for the effect of added sodium chloride upon hydrochloric acid. These points lie along the same straight lines, thus showing that added sodium chloride and added sodium perchlorate have the same effects upon the activity coefficient of hydrochloric acid.

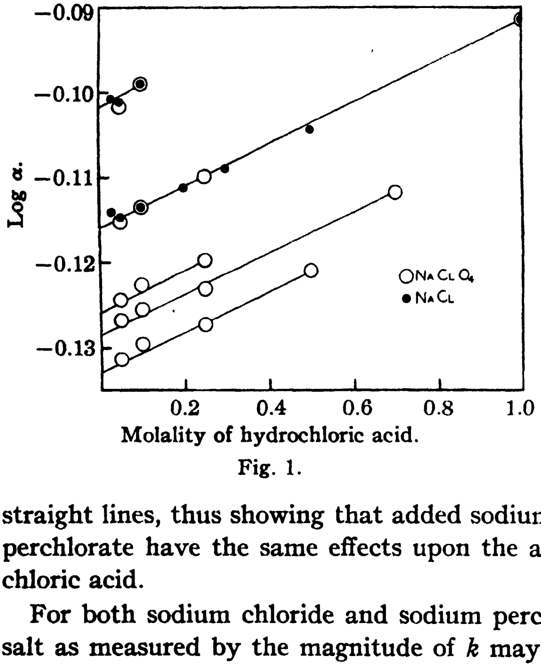

Fig. 1.

For both sodium chloride and sodium perchlorate the effects of added salt as measured by the magnitude of *k* may be somewhat greater at an ionic strength of 0.1 molal than at higher concentrations. Due in part to the small concentration range involved, the slope for this line is more uncertain[2] than that for the other series.

In agreement with the fact that added sodium chloride and sodium perchlorate have substantially the same effect upon the activity coefficients of hydrochloric acid, the few values obtained for the effect of added potassium perchlorate agree closely with those calculated upon the basis of the effect of added potassium chloride.[2] In each case the potassium salt has a greater effect than has the sodium salt.

It might be expected that because sodium chloride and sodium perchlorate have substantially the same effect upon hydrochloric acid, they would have the same effect upon other electrolytes. That this is not the

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(6) Harned and Harris, THIS JOURNAL, 50, 2633 (1928).

case is shown by the results of Bozorth,[7] who determined the effect of added salts including sodium chloride and sodium perchlorate on the solubility of potassium perchlorate. At an ionic strength of 0.5 molal he found that the activity coefficient of potassium perchlorate was about 7% greater in the presence of added sodium chloride than it was in the presence of added sodium perchlorate. It is thus seen that these effects are very specific and hence in general predictions cannot be made with any degree of confidence.

Summary

The effect of added sodium perchlorate, an electrolyte without a common ion, upon the activity of hydrochloric acid at ionic strengths between 0.05 and 1.0 molal and at concentrations of acid from 0.05 to 0.25 molal has been determined by means of electromotive force measurements of the cell H_2, HCl (m_1) + $NaClO_4$ (m_2), AgCl + Ag.

The equation proposed by Harned for solutions of constant ionic strength μ, namely, $\log \alpha = \log \alpha_0 + k(\mu - m)$, holds well for hydrochloric acid in the presence of added sodium perchlorate. The value of the constant k is independent of the ionic strength.

Added sodium perchlorate has, within the range where comparisons are possible, quantitatively the same effect upon the activity coefficient of hydrochloric acid as does added sodium chloride. There is hence no essential difference upon the activity coefficient of hydrochloric acid, between the effect of a salt with a common ion and one without a common ion.

A few measurements were made employing potassium perchlorate as the added salt, but they could not be extensive because of its limited solubility. Within the concentration range investigated, potassium perchlorate has the same effect as has potassium chloride upon the activity of hydrochloric acid.

In general, however, all of these effects are quite specific.

PASADENA, CALIFORNIA

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PUBLISHED OCTOBER 6, 1933

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[7] Bozorth, THIS JOURNAL, **45**, 2653 (1923).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 378]

The Activity Coefficients of Hydrochloric Acid in Aqueous Solutions Containing Either Sodium Dithionate or Perchloric Acid

BY PHILIP G. MURDOCH[1] AND ROBERT C. BARTON

The effect of added salts upon the activity of hydrochloric acid has been studied by a number of investigators.[2] All of these, except Bates and Urmston,[2d] have employed chlorides for the added salts. In the present investigation the influence of the added electrolytes sodium dithionate and perchloric acid was studied, that is, the effect of a negative bivalent ion and that of hydrogen ion were determined. These salts are among the relatively few (except chlorides) which are suitable for this purpose.

The electromotive forces of cells of the type H_2, $HCl(m_1)$ + salt (m_2), AgCl + Ag were determined at 25°. Except where noted the experimental procedures were similar to those of Bates and Urmston.[2d]

The sodium dithionate used was prepared by recrystallizing a C. P. product three times from water. It gave no turbidity with silver nitrate. The salt crystallizes as $Na_2S_2O_6 \cdot 2H_2O$. The proportion of water was determined at intervals and always checked very closely with the calculated value.

The perchloric acid solutions were prepared from the 60% C. P. product of the G. Frederick Smith Corp. It had been redistilled *in vacuo* and was stated to contain not more than 0.004% non-volatile matter. The acid gave no test for chlorides, sulfates or lower oxy-acids.

All mixtures were made up by weight from stock solutions and from solid salt. All concentrations are expressed as moles per 1000 g. of water.

That dissolved air has an effect upon the potential of the calomel electrode in acid solution due to a reaction between mercury, chloride ion, hydrogen ion, and oxygen, has been clearly demonstrated by Randall and Young.[3] The similar effect on the silver–silver chloride electrode is less serious. Güntelberg[2b] found some influence and removed oxygen from his solutions by means of nitrogen. Randall and Young, however, discovered no measurable effect upon silver–silver chloride spiral[4] electrodes in 0.1 *M* hydrochloric acid.

The change in the potential of the silver–silver chloride electrode due to the presence of oxygen is associated with the removal of chloride ion from the solution in immediate contact with the electrode, and is proportional to the fractional change in the activity of the chloride ion. Hence, other factors remaining the same, it is especially noticeable at low chloride concentrations. The removal of the chloride is facilitated by high hydrogen-ion concentrations and therefore increases with increasing acid concentration. Thus with solutions 0.01 *M* in hydrochloric acid and 0.09 *M* in perchloric acid, a decrease of about 1 millivolt was observed when oxygen-free solution was substituted for one which had been in equilibrium with air. With solutions in which the chloride content was 0.1 *M* or greater, the effect was always less than 0.1 millivolt. Hence for those solutions in which the chloride concentration was 0.1 *M* or less, the Linhart type of cell, in which the whole solution is saturated with hydrogen, was employed. Hydrogen was bubbled through the cell for twenty-four hours before introducing the silver-silver chloride electrodes.

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[1] Du Pont Fellow in Chemistry.

[2] (a) Harned, THIS JOURNAL, **38**, 1988 (1916); **42**, 1808 (1920); **48**, 326 (1926); (b) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); (c) Randall and Breckenridge, THIS JOURNAL, **49**, 1435 (1927); (d) Bates and Urmston, *ibid.*, **55**, 4068 (1933).

[3] Randall and Young, *ibid.*, **50**, 989 (1928).

[4] Spiral electrodes may offer less silver surface and hence less opportunity for oxidation than do electrodes employing electrolytic silver crystals. The latter were used by Güntelberg and in this investigation.

Further evidence that a reaction occurs between silver and hydrochloric acid in the presence of air was obtained by shaking a piece of bright silver wire with 0.5 *M* hydrochloric acid for twenty-four hours. At the end of that time the surface of the metal was covered with a characteristic coating of silver chloride which darkened upon exposure to light.

TABLE I

ELECTROMOTIVE FORCES AND ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID

Part A. Effect of Sodium Dithionate

HCl	$Na_2S_2O_6 \times 3$	E. m. f.	Activity coefficient
0.1036[a]	0.0	0.3505	0.795
.1036	.0500	.3521	.771
.1035	.1000	.3531	.756
.1034	.2000	.3544	.738
.1031	.4000	.3557	.722
.1029	.6000	.3564	.714
.1027	.8000	.3565	.714
.1026	.9000	.3561	.720
.1023	1.0500	.3564	(.718)
.1023	1.0500	.3560	.723
.1023	1.1000	.3559	.725
.0500	0.0	.3861	.830
.04997	.0500	.3886	.791
.04991	.1500	.3911	.755
.04985	.2500	.3923	.738
.04973	.4500	.3931	(.728)
.04973	.4500	.3938	.718
.04963	.6500	.3944	.711
.04949	.8500	.3944	.713
.04919	1.4291	.3934	.733

Part B. Effect of Perchloric Acid

HCl	$HClO_4$	E. m. f.	Activity coefficient
0.02498	0.02498	0.40304	0.837
.04821	.04821	.37140	.802
.1493	.1493	.31631	.758
.2570	.2570	.28849	.756
.3732	.3732	.26741	.758
.4961	.4961	.25059	.819
.02143	.03730	.42084	.841
.02445	.07337	.38849	.802
.09885	.2995	.31855	.765
.1881	.5644	.28420	.793
.2482	.7447	.26771	.829
.00988	0.08985	.41072	0.806
.04005	.3604	.34159	.771
.07087	.6378	.31116	.790
.09994	.8995	.29060	.834

[a] The changes in hydrochloric acid concentration result from the water of crystallization present in the sodium dithionate crystals added.

Experimental Results

The measured values of the electromotive forces at 25° and the activity coefficients are given in Table I. For solutions containing sodium dithionate the activity coefficients were computed with the aid of the values for pure hydrochloric acid solutions[5] α_0 by means of the following relation

$$\ln \alpha/\alpha_0 = (F/2RT)\Delta E \qquad (1)$$

Here ΔE is the difference between the electromotive force of the cell containing hydrochloric acid m_1 molal and that containing both hydrochloric acid m_1 molal and added dithionate.

In the case of the perchlorate mixtures such a direct comparison with the values for pure hydrochloric acid solutions is not possible. For such solutions the activity coefficients α were calculated from the equation

$$E - E_0 = -(RT/F)\ln(m_1 + m_2)m_1\alpha^2 \qquad (2)$$

Here m_1 and m_2 are the molal concentrations of the hydrochloric and perchloric acids, respectively; E is the measured electromotive force of the cell containing both acids; E_0 the molal electromotive force for the hydrogen silver–silver chloride cell. Here it is taken as 0.2221 volt.[6]

In Table II the data are shown interpolated to round values of hydrochloric acid and of added electrolyte.

TABLE II

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN PRESENCE OF ADDED SALTS

Ionic strength	Added $Na_2S_2O_6$ HCl molality 0.1	0.5	Added $HClO_4$ Ratio HCl : $HClO_4$ 1:1	1:3	1:9
0.1	0.796	0.791	0.800	0.804	0.809
.2	.757	.754	.769	.773	.780
.5	.722	.719	.761	.767	.773
.7	.714	.712	.779	.787	.792
1.0	.717	.714	.820	.828	.834

Discussion

In general, the results of this and similar investigations must, for the present at any rate, be considered chiefly from the empirical standpoint. On account of the physical complexity of the problem[7] and of mathematical difficulties[8] the treatment of pure electrolytes is, except for very dilute solutions, incomplete and the situation is more complicated in the case of mixtures. However, brief reference will be made to certain relations between the results of this and of other investigations.

In many mixtures of constant ionic strength μ, the activity coefficient α of hydrochloric acid has been found to be related to the concentration m of

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(5) Values which Randall and Young[3] have given for pure hydrochloric acid were used.

(6) Randall and Young.[3] Carmody [THIS JOURNAL, 54, 188 (1932)] has recently arrived at the value 0.2223. Since the values used for the activity coefficients of pure hydrochloric acid are those of Randall and Young, their value of E_0 is employed. The effect of any uncertainty in the values of these investigators is to change all activity coefficients by a constant factor.

(7) Bjerrum, *Trans. Faraday Soc.*, 23, 445 (1927).

(8) Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 350 (1928).

the acid in the mixture and to the activity coefficient α_0 of pure hydrochloric acid at the same ionic strength by the equation.[2a]

$$\log \alpha = \log \alpha_0 + k(\mu - m) \qquad (3)$$

In Fig. 1 are plotted values of log α against those of m at various ionic strengths for the sodium dithionate and perchloric acid mixtures. The above equation demands a linear relation. It will be seen that this relation is closely followed by the dithionate mixtures and is approximately obeyed by the perchloric acid mixtures. The values for the latter mixtures, particularly in dilute solutions, are, however, subject to somewhat greater uncertainty so that for both added electrolytes equation (3) possibly holds within the experimental error. In the case of added sodium dithionate it would appear that k of equation (3) has the same value at different ionic strengths; however, the data are neither sufficiently numerous nor accurate to be certain of this.

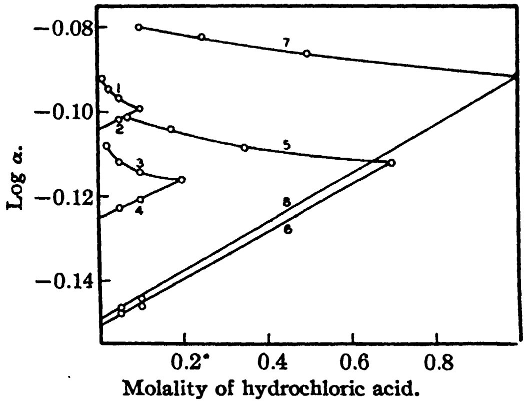

Fig. 1.—Added $HClO_4$: Curve 1, $\mu = 0.1$; Curve 3, $\mu = 0.2$; Curve 5, $\mu = 0.7$; Curve 7, $\mu = 1.0$. Added $Na_2S_2O_6$: Curve 2, $\mu = 0.1$; Curve 4, $\mu = 0.2$; Curve 6, $\mu = 0.7$; Curve 8, $\mu = 1.0$.

Equation (3) has been found to hold for dilute mixtures containing only univalent ions. The results of Randall and Breckenridge[2c] show that it is not followed by mixtures containing barium chloride or lanthanum chloride, but that the similar relation in which m, the concentration of the hydrogen ion constituent, is replaced by the geometric mean molality of the hydrogen and chloride ion constituents does hold. As these authors state, they give no derivation for this rule. Their relation does not hold for the data here presented for perchloric acid. Since equation (3) holds for sodium dithionate solutions, their rule also does also, because for solutions containing no common ion the two relations are identical.

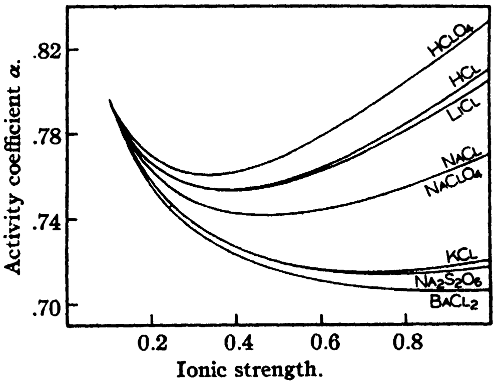

Fig. 2.—Effect of added salts upon 0.1 M HCl.

The comparative effect of increasing amounts of various salts upon the activity coefficient of hydrochloric acid is shown in Fig. 2. Here the activity coefficient of the acid, whose concentration is maintained constant at 0.1 *M*, is plotted against the ionic strength for the added electrolytes, lithium chloride,[2a] sodium chloride,[2a] potassium chloride,[2a] sodium perchlorate,[2d] barium chloride,[2c] sodium dithionate and perchloric acid. The figure shows that, as is to be expected, the minimum value for the activity coefficient is shifted most strongly to higher ionic strengths by those added salts which cause the greatest decrease in its value.

Of these added salts the activity coefficients of lithium chloride, sodium chloride, potassium chloride and barium chloride are known.[9] At a given ionic strength their activity coefficients decrease in the above order. Figure 2 shows that the effects of these salts on hydrochloric acid are in the same order. There is, however, no quantitative relation between the two sets of results. The comparative effects of sodium chloride and potassium chloride are somewhat anomalous since the activity coefficients of potassium chloride in its own pure solutions are but very slightly less than those of sodium chloride, while the activity coefficient of hydrochloric acid in the presence of the former is much less than in the presence of sodium chloride.

For those cases in which the activity coefficients of the salts in their own pure solutions are known, they are less, at the same ionic strength, than are those of hydrochloric acid in the mixture. From this it follows that the hydrogen ion has under certain conditions an unusually large tendency to escape from the solution. Thus, from the closely agreeing data of Harned[2a] and of Güntelberg,[2b] there may be found by extrapolation the activity product $\alpha_H\alpha_{Cl}$ in the solution 0.1 *f* NaCl + 0.0 *f* HCl. Taking the activity coefficient of 0.1 *f* HCl as 0.796 (Ref. 2) this product in 0.1 *f* NaCl is $(0.789)^2$. In this same solution the product $\alpha_{Na}\alpha_{Cl}$ has the value[10] $(0.778)^2$. Hence $\alpha_H/\alpha_{Na} = 1.03$[11] in 0.1 *f* NaCl. That is, the hydrogen-ion constituent has a greater tendency to be "salted out" from 0.1 *f* sodium chloride than has the sodium-ion constituent. This difference is associated with the fact that the electrical forces acting upon these two ions are not the same, though in both cases they are chiefly due to surrounding chloride ions. Thus the mean distances of the chloride ions will be different, for there are involved the diameters of the hydrogen and sodium ions, and the dielectric constant of the medium in their immediate neighborhood. In addition different proportions of these two ion constituents may exist as free ions. The fact that the hydrogen ion has a relatively large activity coefficient may be related to its simple structure. It is less deformable and less polarizable than other ions. The effect is to exert a greater repulsive force and the ion tends to escape from the solution.

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(9) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 362.

(10) Scatchard, THIS JOURNAL, 47, 648 (1925).

(11) Due chiefly to uncertainties in the values for pure hydrochloric acid and pure sodium chloride solutions this figure may be about one per cent. in error.

We wish to acknowledge our indebtedness to Professor S. J. Bates of this Laboratory for much helpful advice and criticism during the course of this investigation.

Summary

The effects of added sodium dithionate and of added perchloric acid upon the activity coefficients of hydrochloric acid in aqueous solution were determined at 25° up to an ionic strength somewhat greater than unity.

The effects of these salts, which are of types not heretofore tested, are qualitatively the same as those of added chlorides of the alkali and alkaline earth elements. Thus, when added to a dilute solution of hydrochloric acid they cause its activity coefficient at first to decrease and then to increase with increasing ionic strength. The addition of perchloric acid increases the activity coefficient more than does that of any other electrolyte. In fact, the activity coefficient in these mixtures is greater than is that of pure hydrochloric acid at the same ionic strength.

The equation which has been found to hold for the effect of certain other electrolytes upon hydrochloric acid, namely, $\log \alpha = \log \alpha_0 + k(\mu - m)$ is closely followed by mixtures containing sodium dithionate and perchloric acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Rate of Addition of Methyl Esters to Trimethylamine[1]

BY LOUIS P. HAMMETT AND HELMUTH L. PFLUGER

We have found that the rate of methylation of trimethylamine to tetramethylammonium ion by the methyl ester of a carboxylic acid is determined by the strength of the acid in a fashion which is without parallel in recorded ester reactions but is very similar to the general acid catalysis equation of Brönsted.[2] The reaction in question: $RCOOCH_3 + N(CH_3)_3 \longrightarrow RCOO' + N(CH_3)_4^+$, is of the same type as those upon which depend the familiar preparative use of the esters of strong acids as alkylating agents; in fact, now that the work of Hantzsch[3] has shown that those acids which are strong, and of equal strength, in aqueous solution are of very different inherent strengths, it becomes apparent that the useful alkylating agents are precisely the esters of the strongest acids, the sulfates, the sulfonates, and, in the order of the strength of the corresponding acids, the halides. That carboxylic esters can accomplish a similar alkylation of tertiary amines was shown by Willstätter and Kahn,[4] who worked without solvent, and merely demonstrated the formation of a large yield of tetraalkylammonium salt. We have found that the reaction goes cleanly and at a suitable rate for measurement in methyl alcoholic solution at 100°.

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[1] This article is based upon a dissertation submitted by Helmuth L. Pfluger to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933. The material was presented at the Washington Meeting of the American Chemical Society, March, 1933.

[2] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924). See the review by Kilpatrick and Kilpatrick; *Chem. Rev.*, **10**, 213 (1932).

[3] Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923).

Materials and Method

Methyl alcohol was synthetic methanol from the Commercial Solvents Corporation. It was dried by the method of Lund and Bjerrum[5] using magnesium in the presence of iodine, and distilled through a bulb stillhead in an all-glass apparatus, retaining only the first two-thirds of the distillate. The product had a density of 0.78691 at 25°, which was not altered by repetition of the treatment. We also tried the method of drying with aluminum amalgam recommended by Hartley and Raikes,[6] but found the co-distillation of mercury with the alcohol troublesome.

Trimethylamine was purchased as a 33% methyl alcohol solution and diluted directly with the purified methyl alcohol. Qualitative tests for primary and secondary amines were negative.

Esters were, in general, purified by extraction of an ether solution with aqueous sodium carbonate, drying over anhydrous sodium sulfate, and distilling through a Vigreux stillhead in an all-glass apparatus, retaining a portion of constant boiling point. *Methyl acetate* was extracted with calcium chloride brine without the use of ether, and then dried and distilled. Boiling points and saponification values were as follows: acetate, 58.9°, 99.6%; benzoate, 198°, 100.2%; *o*-toluate, 212.8°, 99.6%; *p*-toluate, 221°, 99.6%; *o*-chlorobenzoate, 235°, 99.7%; phthalate, 282.3°, 99.2%; *o*-nitrobenzoate, 288°, 99.5%. Free acid was found to be less than 0.01% in all cases except lactate. The *methyl lactate* purchased was a "practical" product and very impure, much of it distilling below 100°. A portion with a constant boiling point of 144.5° after two distillations was used for the velocity measurements. It was still impure, and probably contained a formic ester, as shown by a saponification value 3.75% too high, and by a direct test for formic acid with mercuric oxide in aqueous solution. *Methyl p-nitrobenzoate* was recrystallized from methyl alcohol and melted at 96.5° (corr.).

All materials were kept after purification in stoppered bottles in desiccators containing phosphorus pentoxide.

Method.—The reaction was followed quantitatively by determining the concentration of trimethylamine which remained after definite intervals of time. This was accomplished by steam-distilling the trimethylamine into standard acid and back-titrating with standard alkali. The reaction solutions were prepared by weighing out a suitable amount of ester either directly in a 50-cc. volumetric flask or by use of a small Bailey weight buret, then diluting to the mark with an approximately 0.2 molar solution of trimethylamine in methyl alcohol; 5 cc. of the mixed solution was pipetted into a 50-cc. volumetric flask half full of water (or methyl alcohol, if the ester was insoluble in water) to which 1 cc. of approximately 0.2 *N* hydrochloric acid had previously been added, and the flask was then filled with water up to the mark. This solution was used for the determination of the initial concentration of trimethylamine. The remainder of the reaction mixture was introduced into clean and dry Pyrex ampoules of 8 cc. capacity with the aid of a funnel drawn to a capillary, a small space being left in the ampoule for

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(4) Willstätter and Kahn, *Ber.*, **35**, 2757 (1902).

(5) Lund and Bjerrum, *ibid.*, **64**, 210 (1931).

(6) Hartley and Raikes, *J. Chem. Soc.*, 524 (1925).

expansion of the alcohol upon introduction into the hot bath. The ampoules, cooled by ice, were sealed and introduced into an oil thermostat which operated at 100 ± 0.03°. The time was recorded to the nearest minute.

When an ampoule was removed from the thermostat it was placed immediately in ice and the time was recorded. After cleaning it was opened, its contents were shaken into a small beaker, and 5 cc. was pipetted into an acid solution and diluted to 50 cc. exactly as with the initial reaction mixture.

For the determination of trimethylamine, the micro-Kjeldahl distillation method of Pregl[7] was used. Duplicate determinations were made on each ampoule and on the initial reaction mixture, using for each determination 10 cc. of the solutions diluted as above described. Twenty cc. of standard 0.01 *N* hydrochloric acid diluted to 50 cc. was contained in the receiver. After seven minutes distillation with the condenser immersed below the surface of the acid, followed by four minutes with the tip above the acid solution, the acid was boiled to remove carbon dioxide, and titrated with 0.01 *N* sodium hydroxide from a microburet, using methyl red indicator and a daylight lamp.

Precision.—That the reaction actually produced tetramethylammonium ion in large quantities was demonstrated with all the esters by qualitative test with the potassium bismuth iodide reagent of Kraut. This gives a red precipitate with both trimethylammonium and tetramethylammonium ions, and was therefore applied to a solution which had first been made alkaline and heated to remove the former. It is as a matter of fact difficult to imagine any reaction other than the formation of tetramethylammonium ion by which the quantity of trimethylamine measured by our method of analysis can decrease.

In the case of the nitro compounds a titanous chloride titration showed that no reduction of the nitro group by the alkaline alcoholic solution occurred, and colorimetric tests showed that only traces of nitrite ion were produced by splitting-off of the nitro group during the course of the reaction. In the case of the chlorobenzoate, no chloride ion could be found in the reaction mixture.

In further support of the unique course of the reaction is the failure to observe drifts in the bimolecular constants in nearly all of the reactions studied.

Two successive analyses of the same solution always agreed within three parts per thousand, and usually much better than this. Suitable experiments demonstrated that, within this precision, the operation of introduction into the ampoule and removal from it produced no errors; the distillation method gave figures in agreement with direct titration of a trimethylamine solution; there is no disappearance of trimethylamine when a methyl alcoholic solution is heated at 100° for one month.

Table I contains the detailed experimental data for two esters, methyl acetate and methyl benzoate. Except for the two nitrobenzoates, the precision and freedom from drift here exhibited is typical, as may be seen from the average deviations included in Table III. In the case of *p*-nitro-

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(7) Pregl, "Quantitative Organic Microanalysis," translated by Fyleman, P. Blakiston's Son & Co., Philadelphia, p. 94 ff.

benzoate, the much larger and entirely irregular scatter of the results probably arises from the difficulty of manipulation without loss of solutions in a volatile solvent of this not very soluble substance. In the case of *o*-nitrobenzoate, and in this case only, was there the sort of recognizable drift of the constants apparent in Table II. The constants for methyl

TABLE I

METHYL BENZOATE

Run 1. Initial concn. of ester, 0.6170 m. p. l.

Time, hrs.	0	122	144	178	310
Concn. of $(CH_3)_3N$	0.1928	0.06736	0.05560	0.04395	0.01699
$k \times 10^2$	....	1.593	1.624	1.593	1.593

Run 2. Initial concn. of ester, 0.5778 m. p. l.

Time, hrs.	0	119	139	305
Concn. of $(CH_3)_3N$	0.1935	0.07307	0.06275	0.02039
$k \times 10^2$	.....	1.619	1.628	1.616

METHYL ACETATE

Run 1. Initial concn. of ester, 0.5178 m. p. l.

Time, hrs.	0	144	210	224	320	390
Concn. of $(CH_3)_3N$	0.1962	0.1297	0.1094	0.1058	0.0846	0.0710
$k \times 10^3$	....	5.959	5.933	5.908	5.816	5.900

Run 2. Initial concn. of ester, 0.5021 m. p. l.

Time, hrs.	0	148	210	231	261
Concn. of $(CH_3)_3N$	0.1962	0.1300	0.1103	0.1055	0.0978
$k \times 10^3$	....	5.970	6.043	5.823	5.986

TABLE II

METHYL *o*-NITROBENZOATE

Run 1. Initial concn. of ester, 0.1873 m. p. l.

Time, hrs.	0	3.25	6	12	24
Concn. of $(CH_3)_3N$	0.1729	0.1441	0.1278	0.1022	0.0735
k	....	.3258	.3098	.2998	.2864

Run 2. Initial concn. of ester, 0.1413 m. p. l.

Time, hrs.	0	12	30.2	35.5
Concn. of $(CH_3)_3N$	0.1720	0.1162	0.0848	0.0795
k	....	.2991	.2722	.2675

TABLE III

	Alkylation constants	Ionization constants 25°	99°	Hydrolysis constants
Acetate	0.00593 ± 0.00006	0.0000186	0.000011	100
p-Toluate	.0123 ± .0003	.000044	.000032	12.1
Benzoate	.01609 ± .00014	.000068	.000045	25.9
o-Toluate	.0166 ± .0003	.000135	.000058	....
Lactate	.0351 ± .0009	.000138	.....	968
o-Chlorobenzoate	.0727 ± .0014	.00132	.00042	49.5
p-Nitrobenzoate	.113 ± .013	.000396	.....	2690
Phthalate	.1243 ± .0017	.000654	.....	....
o-Nitrobenzoate	.33 (extrapolated)	.0065	.00161	148

lactate also show a drift if the actual initial concentrations of ester and amine are used in the calculation, a fact which we attribute to the impurity already mentioned. If, however, those concentrations found to exist after some five or ten per cent. of the ester has reacted are used as a starting point, the excellent agreement indicated by the average deviation shown is obtained.

Conclusions

The mean values of the rate constants of the nine carboxylic esters investigated in this research are arranged in Table III in the order of their magnitude. There are also included the dissociation constants[8] of the corresponding acids at 25°, and those reported by Schaller[9] for benzoic acid and its derivatives at 99°, and by Noyes[10] for acetic acid at 100°. These ionization constants are, of course, the values obtaining in aqueous solution.

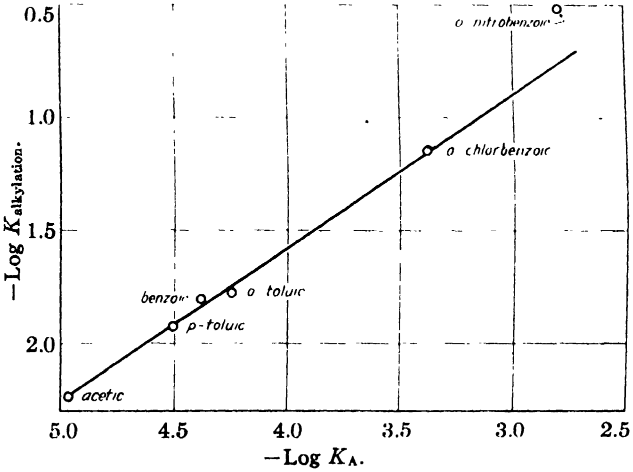

Fig. 1.

It is obvious that the rate of methylation of trimethylamine by these esters increases with increasing strength of the corresponding acid. But the relationship between reaction rate and acid strength is more than qualitative. Figure 1 contains a plot of the logarithm of the rate constant against the logarithm of the dissociation constant of the corresponding acid at either 100 or 99°, for all of the esters studied for whose acids dissociation constants at this temperature are available. The straight line whose equation is $\log k_v = 1.10 + 0.67 \log K_A$, where k_v is the velocity constant of the alkylation reaction, and K_A is the acid ionization con-

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(8) Where no specific references are given, the dissociation constants have been obtained from the "International Critical Tables." Attention is called, however, to an error in the order of magnitude given in these tables for the constant of benzoic acid.

(9) Schaller, *Z. physik. Chem.*, **26**, 497 (1898).

(10) Noyes, THIS JOURNAL, **30**, 335 (1908).

stant, fits these data excellently except in the case of *o*-nitrobenzoate. The deviation of almost 0.3 unit in this case requires further investigation.

In Fig. 2 the alkylation constants at 100° have been plotted against acid dissociation constants at 25°. This seems a more reasonable procedure than the estimation of temperature coefficients which are at present unknown. It is clear that there is a very definite advantage in the comparison of the alkylation velocity at 100° with the ionization constant of the acid at the same temperature, especially when ortho substituted benzoic acids are concerned. The fact that the latter have especially large temperature coefficients of ionization has been pointed out by Smallwood[11] and given a theoretical derivation.

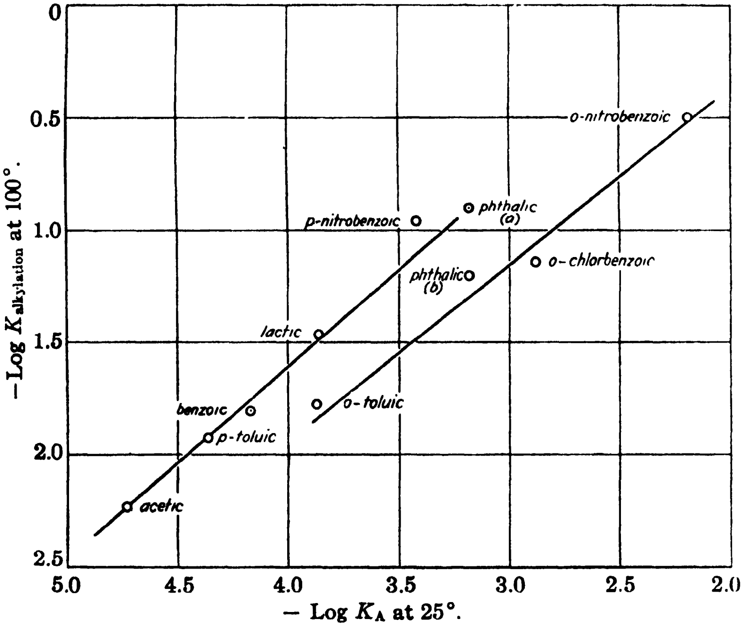

Fig. 2.

The acid with whose ionization constant the alkylation velocity of dimethyl phthalate is to be compared is of course the monomethyl ester of phthalic acid, and it is this constant which is listed in Table III. If the alkylation rate is plotted against this, the point (*a*) in Fig. 2 is obtained. Since, however, the dimethyl ester has twice the probability of reacting that a monomethyl ester would have, it is reasonable to divide the rate constant by two for comparison with the esters of monobasic acids. If this is done, point (*b*), which is in reasonable agreement with the other ortho substituted esters, is obtained.

We shall report later on the behavior of phenolic esters which do methyl-

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(11) Smallwood, THIS JOURNAL, 54, 3048 (1932).

ate trimethylamine, but do not exhibit the same relation between rate and acid strength as that found for carboxylic esters, and upon the closely related problem inherent in the fact that we have here compared velocities in methyl alcohol solution with acid strengths in aqueous solution. This relation appears in the fact that carboxylic and phenolic acids are very differently affected by a change in solvent.[12]

Discussion

Because there is no universally valid relation between the rate of a chemical reaction and the equilibrium constant of the same or closely related reactions,[13] and because there is indeed no obvious reason to expect it, the existence of a simple and unique relation in this case presents a striking contrast which throws light on a number of important problems of reaction mechanism.

If one attempts to relate the velocity of the reaction of an ester with hydroxyl ion, *i. e.*, its alkaline hydrolysis, to the strength of the corresponding acid in the same way as we have done with the velocity of the reaction with trimethylamine, one obtains the complete lack of functional relationship exhibited by Fig. 3. The data[14] necessary are included in Table III. There is nevertheless this regularity in the large amount of existing data on hydrolysis velocities: that any substitution, of whatever electrochemical nature, in the immediate neighborhood of the carboxyl group tends to decrease the hydrolysis rate.[15] Whether the mechanism implied by the usual name "steric hindrance" is correct or not, the facts are that ethyl benzoate hydrolyzes only one-fourth as fast as ethyl acetate, though benzoic acid is almost four times as strong as acetic acid; and that alpha substituted aliphatic esters and ortho substituted aromatic esters hydrolyze less rapidly than unsubstituted esters of the same strength or esters containing the same substituent in a position further removed from the carboxyl group.

An important difference in principle between the reaction of an ester with a tertiary amine and its reaction with hydroxyl ion appears in the fact that the ester must in the first case break thus, $R_1COO\vdots R_2$, at the dotted line, both oxygens going with the acid radical, whereas the hydrolysis may go by two quite different mechanisms

$$R_1COO\vdots R_2 + OH' \longrightarrow R_2OH + R_1COO' \qquad (I)$$

$$R_1CO\vdots OR_2 + OH' \longrightarrow R_1COOH + 'OR_2 \qquad (II)$$

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[12] Larsson, Dissertation, Lund, 1924.

[13] Adkins and Adams, THIS JOURNAL, 47, 1368 (1925); Conant, *Ind. Eng. Chem.*, 24, 470 (1932).

[14] These data are for the hydrolysis of ethyl esters, and are taken from Olsson's tables in which *k* for ethyl acetate is arbitrarily set at 100 [Olsson, *Z. physik. Chem.*, 133, 233 (1928)] or calculated to the same scale from Kindler's tables [*Ann.*, 450, 1 (1926); 452, 90 (1927); 464, 278 (1928)]. The use of ethyl esters is entirely justified by the well-demonstrated constancy of the ratio of the hydrolysis constants of ethyl and methyl esters [see Olsson, p. 240) and the wider range of data available for the ethyl esters.

[15] See for instance Kindler, *Ann.*, 464, 278 (1928).

In the first case, the reaction may be called an alkylation of the hydroxyl ion, and in the second case an acylation, the acylation of ammonia to acetamide by methyl acetate being entirely analogous. It has been a much discussed problem for some thirty years whether the one or the other or both of these mechanisms agrees more closely with the facts.[16] If the hydrolysis mechanism were the alkylation represented by equation I, it is inconceivable that it should be more subject to steric hindrance than is the alkylation of trimethylamine. The existence of steric effects in the hydrolysis compared with their complete absence in the amine reaction is therefore strong evidence that the hydrolysis is an acylation proceeding according to equation II, the break occurring at a point in the molecule nearer the hindering groups than would be the case with the alkylation.

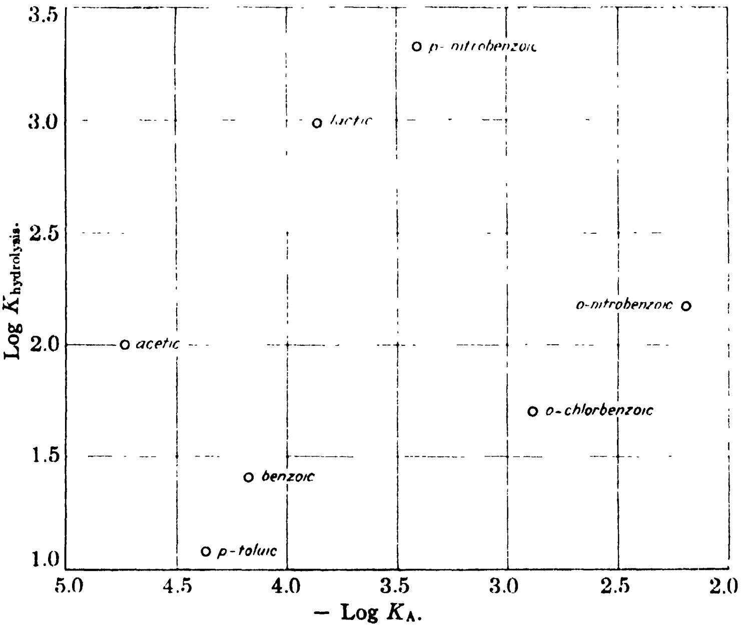

Fig. 3.

The previously existing evidence favors this mechanism for the hydrolysis of carboxylic esters, but it is directly applicable only to esters of secondary and tertiary alcohols. Holmberg[17] in 1912 pointed out that a Walden inversion can occur in the hydrolysis of an optically active alcohol whose activity depends upon an asymmetric carbinol carbon only if the hydrolysis is an alkylation, and follows mechanism I. Such an inversion has never been observed in the esterification and subsequent hydrolysis of a carboxylic ester.[16,17,18] On the other hand, the existence of an inversion

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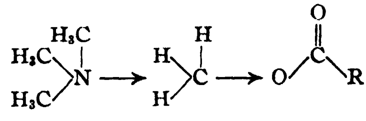
(16) Hückel and Frank, *Ann.*, **477**, 137 (1930).

(17) Holmberg, *Ber.*, **45**, 2997 (1912).

(18) Fischer, *Ann.*, **394**, 360 (1912); Verkade, *ibid.*, **477**, 287, 297 (1930).

in the hydrolysis of *p*-toluene sulfonic esters[19] of active alcohols proves that these do hydrolyze by mechanism I, a reasonable result because these esters of strong acids are in general active alkylating agents.[20] In further agreement is the fact that steric hindrances due to ortho substitution do not appear in the hydrolysis of substituted benzene sulfonic esters.[21]

With respect to detailed mechanism, it is profitable to consider the amine reaction as a substitution of trimethylamine for acetate ion, both amine and ion being bases in the Brönsted sense or molecules with lone electron pairs in the Lewis picture. Of the two widely discussed mechanisms for substitution reactions, the one dependent upon a preliminary dissociation of one reactant is here impossible. It would require either that the rate be independent of nature and concentration of the base or that it be proportional directly to the dissociation constant and inversely to the concentration of the acid ion produced. The hypothesis of a preliminary addition reaction on the other hand can be reconciled with the present result only by supposing that the rate of the addition is dependent upon the strength of a linkage which is to be broken in a further reaction of the addition compound. Recently, however, a theory of simultaneous addition and dissociation has been proposed on quantum mechanical grounds by London,[22] given quantitative application to simple reactions by Eyring and Polanyi,[23] and by Eyring and others,[24] and utilized qualitatively for more complex reactions by Polanyi[25] and others and by Olson.[26] Applied to the methylation of trimethylamine, one obtains the picture shown, in which the arrows represent the direction of motion. The reaction takes place by the approach of the nitrogen of the pyramidal trimethylamine molecule to the carbon of the methyl group on the side directly opposite to the oxygen atom. Simultaneously the oxygen and the accompanying acid radical recede from the carbon. If the kinetic energy of the approaching trimethylamine exceeds a certain minimum, the activation energy of the reaction, there is complete ejection of the acid ion, attachment of the trimethylamine, and rearrangement of the hydrogens on the methyl to new positions of equilibrium. The activation energy is dependent upon the energies of both the broken bond and the newly formed one, increases very rapidly with any deviation from linearity of ap-



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(19) Phillips, *J. Chem. Soc.*, **123**, 44 (1923); Kenyon, Phillips and Turley, *ibid.*, **127**, 899 (1925).

(20) Ferns and Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

(21) Demény, *Rec. trav. chim.*, **50**, 60 (1931).

(22) London, *Z. Elektrochem.*, **35**, 552 (1929).

(23) Eyring and Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931).

(24) Eyring, THIS JOURNAL, **53**, 2537 (1931); Rollefson and Eyring, *ibid.*, **54**, 170 (1932); Eyring, *ibid.*, **54**, 3191 (1932); Kimball and Eyring, *ibid.*, **54**, 3876 (1932).

(25) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); Bergmann, Polanyi and Szabo, *ibid.*, **B20**, 161 (1933).

(26) Olson, *J. Chem. Phys.*, **1**, 418 (1933).

proach,[23,24] and determines the reaction velocity provided steric factors are constant. One need only suppose that the energy of the bond between alkyl and acid radical is related to the strength of the corresponding acid to obtain a reasonable account of the existence if not of the exact form of a relation between velocity and acid strength. The equally probable dependence upon the strength of the reacting base is much more likely to be complicated by steric effects, and both base strength and spatial configuration are apparently factors in determining the rate of addition of different tertiary amines to a single alkyl halide.[27]

In further agreement with the demonstrated properties of the alkylation reaction, a Walden inversion must take place when the carbinol carbon is asymmetric[25,26] and variations in shape or size of the radical R can have no effect as such upon the velocity of a reaction which takes place at a point in the molecule so widely separated from R and so completely shielded from it.

The formal identity of the relation here found between acid strength and methylation rate with that found by Brönsted[2] between acid strength and the rate of a reaction subject to general acid catalysis suggests a fundamental similarity in the two reactions. It is therefore probable that the rate-determining step in the catalysis is a transfer of hydrogen ion from the acid HA to the weakly basic substrate S, entirely analogous to the transfer of methyl in the alkylation reaction $HA + S \rightleftarrows SH^+ + A'$, and that the further reaction of the ion SH^+ is by comparison extremely rapid. This is the interpretation of the catalysis suggested by Pedersen,[28] and it may be added that the mechanism of reaction just discussed casts considerable doubt upon the possibility of further dissection of the reaction, for instance, into the formation of an addition compound (HA, S), and its subsequent further reaction. Those predictions of a dependence upon base strength as well as upon acid strength and upon steric properties which were made for the alkylation reaction should be equally applicable to both acid and basic catalysis and should furnish a test of the usefulness of the interpretation.

Summary

It has been found that the rate of the alkylation of trimethylamine to tetramethylammonium ion by the methyl ester of a carboxylic acid is related to the strength of the acid by an equation of the same form as that which connects the rate of a reaction subject to general acid catalysis with the strength of the catalyst acid.

The complete absence of steric hindrances in this reaction compared with its predominance in ester hydrolysis shows that the mechanisms of the two reactions are different.

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[27] Preston and Jones, *J. Chem. Soc.*, **101**, 1930 (1912); Thomas, *ibid.*, **103**, 594 (1913).

[28] Pedersen, THIS JOURNAL, **53**, 18 (1931).

It is probable that the rate-determining step in the general acid and basic catalysis of Brönsted is a transfer of hydrogen ion from acid catalyst to substrate similar to the transfer of methyl in the alkylation reaction.

These results are in agreement with the theory of simultaneous addition and dissociation in substitution reactions.

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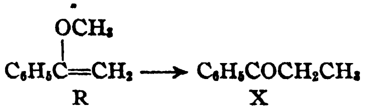
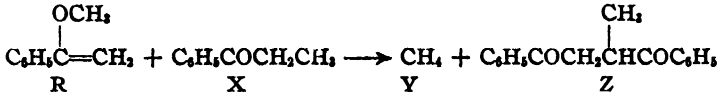
The Kinetics of the Rearrangement of α-Methoxystyrene[1]

BY F. H. MACDOUGALL, WALTER M. LAUER AND MARVIN A. SPIELMAN[2]

Claisen[3] has shown that α-methoxystyrene undergoes on heating a molecular rearrangement with the formation of propiophenone. A recent investigation[4] of the process has revealed an unusual type of side reaction. The unchanged starting material (R) reacts with the rearrangement product (X); a molecule of methane (Y) is eliminated and 1,2-dibenzoylpropane (Z) results.



$$\underset{R}{C_6H_5\overset{OCH_3}{\overset{|}{C}}=CH_2} \longrightarrow \underset{X}{C_6H_5COCH_2CH_3} \qquad \text{I}$$



$$\underset{R}{C_6H_5\overset{OCH_3}{\overset{|}{C}}=CH_2} + \underset{X}{C_6H_5COCH_2CH_3} \longrightarrow \underset{Y}{CH_4} + \underset{Z}{C_6H_5COCH_2\overset{CH_3}{\overset{|}{C}}HCOC_6H_5} \qquad \text{II}$$

In connection with a study of the mechanism of this type of molecular rearrangement, it became desirable to know the order of the reaction and to gain as much information as possible about the unique condensation reaction (II). While the mixture of compounds resulting from reactions I and II does not lend itself to highly precise methods of analysis, nevertheless a technique was developed whereby its composition could be determined with a fair degree of accuracy.

Experimental Methods

The thermostat was an upright Pyrex tube, 16 × 40 cm. rounded at the lower end and closed at the top with an asbestos cover. The lower two-thirds was wrapped with an asbestos jacket. Within was suspended a cylindrical aluminum block, 4.5 × 9 cm., in which were drilled five holes. An 8 mm. hole through the center bore a glass supporting rod and symmetrically disposed about it were four cylindrical holes. The diameter

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(1) This paper is a portion of the thesis presented by Marvin A. Spielman to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Dupont Research Fellow in Chemistry, 1932–1933.

(3) Claisen, *Ber.*, **29**, 2931 (1896); Claisen and Haase, *ibid.*, **33**, 3778 (1900).

(4) Lauer and Spielman, THIS JOURNAL, **55**, in press (1933).

of these was 10 mm. except near the bottom where the bore was smaller. Three of these holes held the sample tubes; the fourth hole held a thermometer. A constant temperature was maintained by boiling about 50 cc. of an appropriate liquid at such a rate that the vapor condensed well above the aluminum block at a marked position above the insulating jacket. The following liquids were used: diphenyl ether, b. p. 260.0 ± 0.3°; isosafral, b. p. 249.5 ± 0.4°; quinoline, b. p. 235.6 ± 0.5°; and methyl salicylate, b. p. 222.8 ± 0.6°. Temperature measurements were made with Anschütz standard thermometers which were checked against instruments having Bureau of Standards calibrations.

Samples (about 0.8 g.) of freshly distilled, analytically pure α-methoxystyrene were weighed out into 8-cm. lengths of 8-mm. glass tubing sealed at one end. These were filled with nitrogen, loosely stoppered and drawn out to 8-cm. capillaries which were sealed after room temperature was reached. The liquid occupied about 80% of the volume of the reaction vessels. Calculation shows that, even at the highest temperature employed less than one per cent. of the material is in the gas phase. The tip was formed into a hook through which a light wire was passed to facilitate handling. After they were removed from the thermostat, they were cooled and unsealed in a closed system connected to a gas buret. Heating with a boiling water-bath served to expel the dissolved methane. After cooling to room temperature, the volume of gas was determined over mercury. The heating with the water-bath and the subsequent cooling were repeated until constant values were obtained for the volume of gas.

The residual liquid was then removed and analyzed for the methoxyl group by the Zeisel method, using the elegant volumetric modification of the method described by Viebock and Schwappach.[5] In these determinations, check analyses were made and only those were used which agreed to within 0.2% OCH_3. The percentages of α-methoxystyrene so obtained are probably correct to within one per cent. In the measurement of the methane, gas buret readings could be duplicated to 0.01 cc. after heating and cooling, but the total volume of methane was in general small and there was always the danger that some of the methane might have been retained in the organic liquid.

We see from reaction equations I and II that, so long as all the methane formed remains in the liquid, there is no change in the total number of molecules. The composition of the reaction mixture is expressed in mole fractions assuming all the methane to be dissolved. Since in general the amount of methane formed is small, this procedure is sufficiently accurate.

Since some time is required to heat the reacting substance to the temperature selected for the experiment, a time correction is necessary. This was determined graphically by plotting values of $1/R$ against the time and extrapolating back to a value of R equal to 1. The time correction was found to be three minutes. Accordingly all time values have been diminished by this amount.

For fuller details about experimental methods, the paper by Lauer and Spielman[4] may be consulted.

Kinetic Equations.—Let R, X and Y be the mole fractions of α-methoxystyrene, propiophenone and methane, respectively, in the reaction mixture at any time t. We shall show that reactions I and II are of the second order. On this basis, we have the following set of equations:

$$dR/dt = -k_1R^2 - k_2RX \qquad (1) \qquad dY/dt = k_2RX \qquad (3)$$

$$dX/dt = k_1R^2 - k_2RX \qquad (2) \qquad 1 = R + X + 2Y \qquad (4)$$

Of the equations (1), (2) and (3), only two are independent, because of the

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(5) Viebock and Schwappach, *Ber.*, **63**, 2818 (1930).

relation expressed in equation (4). It will be convenient to make the substitutions

$$u = k_1 t \qquad (5) \qquad\qquad c = k_2/k_1 \qquad (6)$$

Equations (1), (2) and (3) become

$$\mathrm{d}R/\mathrm{d}u = -R^2 - cRX \qquad (7) \qquad\qquad \mathrm{d}Y/\mathrm{d}u = cRX \qquad (9)$$
$$\mathrm{d}X/\mathrm{d}u = R^2 - cRX \qquad (8)$$

R, X and Y are functions of u (or t) but cannot be expressed in terms of any simple function of u containing a finite number of terms. They can, however, be represented by infinite power series. The coefficients of the powers of u in the various series can be found by assuming an expansion $R = a_0 + a_1u + a_2u^2\ldots$ and $X = b_0 + b_1u + b_2u^2\ldots$ Substitution of these expressions in (7) and (8) leads to a knowledge of the coefficients. A less tedious method employs Maclaurin's theorem. If we denote the value of a function for $u = 0$ by the subscript zero, we have

$$R = R_0 + u(\mathrm{d}R/\mathrm{d}u)_0 + u^2/2!\,(\mathrm{d}^2R/\mathrm{d}u^2)_0 + u^3/3!\,(\mathrm{d}^3R/\mathrm{d}u^3)_0 + \ldots \qquad (10)$$
$$X = X_0 + u(\mathrm{d}X/\mathrm{d}u)_0 + u^2/2!\,(\mathrm{d}^2X/\mathrm{d}u)_0 + u^3/3!\,(\mathrm{d}^3X/\mathrm{d}u^3)_0 + \ldots \qquad (11)$$

Restricting ourselves to the case in which we start our reaction with pure α-methoxystyrene, we readily obtain from (4) and by repeated differentiation of (7) and (8) the results

$$R_0 = 1;\ (\mathrm{d}R/\mathrm{d}u)_0 = -1;\ (\mathrm{d}^2R/\mathrm{d}u^2)_0 = 2 - c;\ (\mathrm{d}^3R/\mathrm{d}u^3)_0 = -6 + 6c + c^2;$$
$$(\mathrm{d}^4R/\mathrm{d}u^4)_0 = 24 - 36c - 4c^2 - c^3;\ \ (\mathrm{d}^5R/\mathrm{d}u^5)_0 = -120 + 240c - 6c^2 - 4c^3 + c^4;$$
$$X_0 = 0;\ (\mathrm{d}X/\mathrm{d}u)_0 = 1;\ (\mathrm{d}^2X/\mathrm{d}u^2)_0 = -2 - c;\ (\mathrm{d}^3X/\mathrm{d}u^3)_0 = 6 + 2c + c^2$$
$$(\mathrm{d}^4X/\mathrm{d}u^4)_0 = -24 - c^3;\ (\mathrm{d}^5X/\mathrm{d}u^5)_0 = 120 - 48c - 26c^2 - 8c^3 + c^4$$

Similar procedures enable us to express in a power series in u any function of R or X, *e. g.*, $1/R$ and $1/(R+Y)$. We thus obtain the expansions

$$1/R = 1 + u + \frac{c}{2}u^2 - \frac{c^2}{6}u^3 + \frac{2c^2 + c^3}{24}u^4 - \frac{4c^2 + 6c^3 + c^4}{120}u^5 + \ldots \qquad (12)$$

$$1/(R + Y) = 1 + u - \frac{c}{3}u^3 + \frac{2c + 2c^2}{24}u^4 \ldots \qquad (13)$$

$$R = 1 - u + \frac{2 - c}{2}u^2 - \frac{6 - 6c - c^2}{6}u^3 + \frac{24 - 36c - 4c^2 - c^3}{24}u^4 + \ldots \qquad (14)$$

$$X = u - \frac{2 + c}{2}u^2 + \frac{6 + 2c + c^2}{6}u^3 - \frac{24 + c^3}{24}u^4 \ldots \qquad (15)$$

$$Y = \frac{c}{2}u^2 - \frac{4c + c^2}{6}u^3 + \frac{18c + 2c^2 + c^3}{24}u^4 \ldots \qquad (15a)$$

It will be shown that the value of $c = k_2/k_1$ is about 1/8. If we plot $1/R$ and $1/(R+Y)$ against u (or t), we shall obtain in the first place a curve which approximates to a straight line for small values of u but curves upward for larger values of u. In the second place (for the $1/(R+Y)$ curve), the curve will be more nearly straight over a greater range of u but should be slightly concave to the u axis. In Fig. 1 are plotted values of $1/R$ and $1/(R+Y)$ against t for the reaction at 260°. It will be seen that the curves for $1/R$ and $1/(R+Y)$ exhibit the predicted behavior. Figure 2 gives a graphic picture of the rate of formation of methane.

Equations (14) and (15) represent the values of R and of X, respectively, only for values of u less than unity. In all our experiments, the study of the reaction was extended to times for which u was greater than 2. These equations therefore can be applied only in the earlier stages of the reaction.

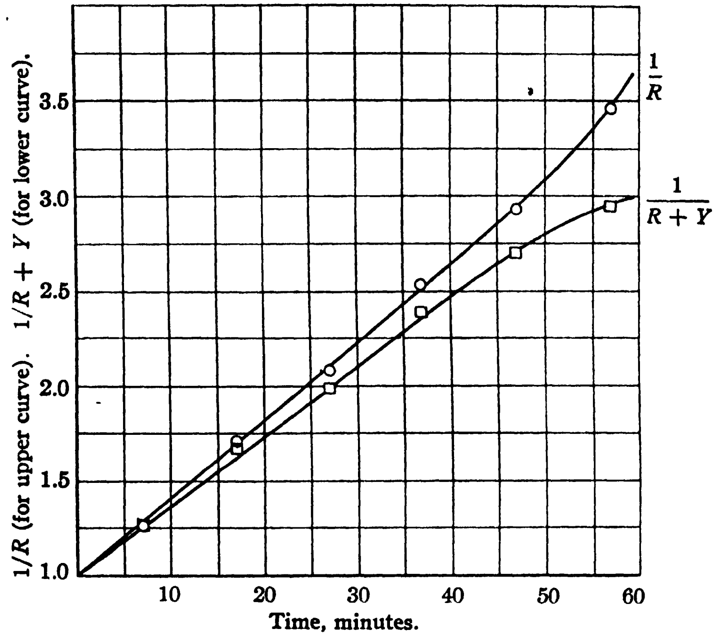

Fig. 1.—Decomposition of α-methoxystyrene at 260.0°.

In order to be able to determine the best values of k_1 and k_2 using all the data for a run at a given temperature it seemed desirable to express R and X in a power series such that the series would be convergent and have a definite finite limit for all values of the variable. This was accomplished in the following way. Introducing the new variable V defined by the equation

$$V = u/(1 + u) \tag{16}$$

we see that $V = 0$ for $u = 0$ and that $V < 1$ for all finite values of u (or t). On substitution, the fundamental equations (7) and (8) become

$$(1 - V)^2\, dR/dV = -R^2 - cRX \tag{17}$$

$$(1 - V)^2\, dX/dV = R^2 - cRX \tag{18}$$

Applying Maclaurin's theorem, we can express R and X and any function of them in a power series in V. We obtain

$$R = 1 - V - \frac{c}{2}V^2 + \frac{c^2}{6}V^3 + \frac{c^2}{3}\left(1 - \frac{c}{8}\right)V^4 + \frac{17}{60}c^2\left(1 - \frac{12}{17}c + \frac{c^2}{34}\right)V^5 + \ldots \tag{19}$$

$$X = V - \frac{c}{2}V^2 - \frac{2}{3}c\left(1 - \frac{c}{4}\right)V^3 - \frac{c}{2}\left(1 - c + \frac{c^2}{12}\right)V^4 - \frac{2}{5}c\left(1 - \frac{47}{24}c + \frac{7}{12}c^2 - \frac{c^3}{48}\right)V^5 \ldots \quad (20)$$

$$Y = \frac{c}{2}V^2 + \frac{c}{3}\left(1 - \frac{c}{2}\right)V^3 + \frac{c}{4}\left(1 - \frac{5}{3}c + \frac{c^2}{6}\right)V^4 + \frac{c}{5}\left(1 - \frac{8}{3}c + \frac{13}{12}c^2 - \frac{c^3}{24}\right)V^5 \ldots \quad (21)$$

$$X + Y = \frac{1 - R + X}{2} = V - \frac{c}{3}V^3 - \frac{c}{4}\left(1 - \frac{c}{3}\right)V^4 + \frac{c}{5}\left(1 - \frac{5}{4}c + \frac{1}{12}c^2\right)V^5 \quad (22)$$

The greatest value of V met with in our experiments was about two-thirds. Moreover, the value of c was found to be of the order of one-eighth. Accordingly we proceeded as follows. Assuming an approximate value of c and using the experimentally determined values of X and Y for a given time t, an approximate value of V was easily calculated by means of equation (22). Substituting this value of V in equation (19), a more accurate value of c was determined. Using this value of c in equation (22), there resulted a more accurate value of V and on substitution once more in equation (19), we obtained a final value of c. This procedure was gone through for all the data of a run at a given temperature. From the values of V thus obtained for the various times t, equation (16) gave the cor-

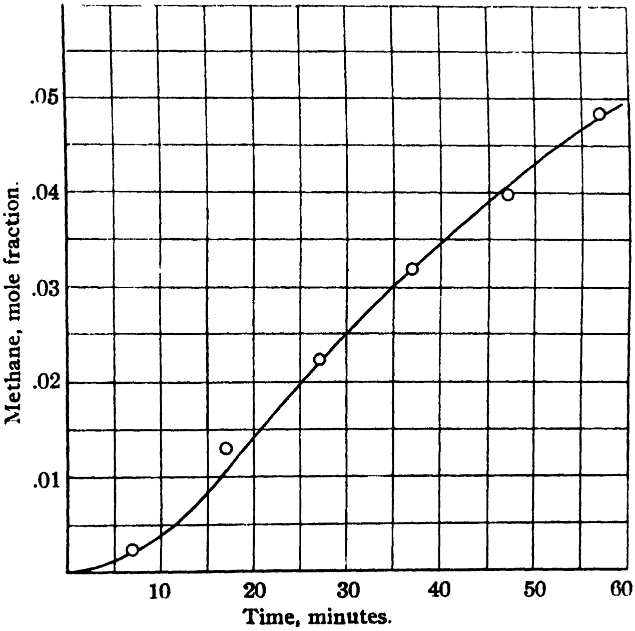

Fig. 2.—Condensation reaction at 260.0°.

responding values of u and hence the values of k_1 (equation (5)). In Table I are given the results of these calculations applied to the data obtained at 260°.

TABLE I

260°

t (corr.), min.	R	X	Y	c	V	u	k_1	k_2
7	0.7963	0.1989	0.0024	[0.100]	0.2017	0.2527	0.0361	
17	.5888	.3850	.0131	.123	.4017	.6714	.0395	
27	.4800	.4752	.0224	.124	.5051	1.021	.0378	
37	.3950	.5414	.0318	.126	5851	1.410	.0381	
47	.3413	.5791	.0397	.133	.6342	1.734	.0369	
57	.2989	.6134	.0484	.122	.6760	2.086	.0366	
			Av.	0.126			0.0375	0.00473

As additional evidence in regard to the correctness of our fundamental equations, we give in Table II the values of R and of Y calculated by means of equations (19) and (21), assuming $k_1 = 0.0375$; $c = 0.126$ and $k_2 =$

TABLE II

CALCULATION OF R AND Y AT 260°

$k_1 = 0.0375$; $c = 0.126$; $k_2 = 0.00473$

t, min.	7	17	27	37	47	57
R, obs.	0.7963	0.5888	0.4800	0.3950	0.3413	0.2989
R, calcd.	.7894	.6015	.4817	.3989	3383	.2920
Y, obs.	.0024	.0131	.0224	.0318	.0397	.0484
Y, calcd.	.0031	.0126	.0231	.0330	.0418	.0496

TABLE III

REACTION AT 249.5°

t (corr.), min.	R	X	Y	c	k_1	k_2
12	0.8284	0.1676	0.0020	0.138	0.0170	
27	.6799	.3055	.0073	.120	.0170	
42	.5610	.4192	.0099	[.067]	.0182	
57	.4567	.4981	.0226	.108	.0197	
72	.4123	.5317	.0280	.122	.0184	
87	.3350	.5914	.0368	.125	.0207	
102	.3007	.6117	.0438	.135	.0201	
			Av.	0.125	0.0187	0.00234

TABLE IV

REACTION AT 235.6°

t (corr.), min.	R	X	Y	c	k_1	k_2
27	0.8231	0.1725	0.0022	0.132	0.00785	
57	.6983	.2893	.0062	.114	.00740	
87	.5613	.4117	.0135	.106	.00864	
117	.4473	.5011	.0258	.132	.00982	
147	.4041	.5317	.0321	.144	.00914	
177	.3561	.5701	.0369	.137	.00918	
			Av.	0.128	0.00867	0.00111

0.00473. The agreement between calculated and observed values is very satisfactory.

Tables III and IV give the results obtained from the experiments at 249.5 and 235.6°.

Experiments at 222.8 °C.—At the temperature 222.8° a run was made starting with approximately equivalent amounts of α-methoxystyrene and propiophenone. Representing by a the mole fraction of α-methoxystyrene at the beginning of the reaction, we obtain as solutions in series of equations (17) and (18)

$$\begin{aligned} R/a = {} & 1 - [a + (1 - a)c]V - \left[a - a^2 + \left(\frac{2 - 5a + 4a^2}{2}\right)c - \right. \\ & \left.\left(\frac{1 - a}{2}\right)c^2\right]V^2 - \left[a\,(1 - a)^2 + (1 - 4a + 6a^2 - 3a^3)\,c - \right. \\ & \left.\frac{(6 - 13a + 14a^2 - 6a^3)}{6}c^2 + \frac{(1 + a - 4a^2 + 2a^3)}{6}c^3\right]V^3 + \ldots \end{aligned}$$

$$\begin{aligned} X/a = {} & \frac{1 - a}{a} + [a - (1 - a)\,c]V + \left[a - a^2 - \left(\frac{2 - a}{2}\right)c + \right. \\ & \left.\left(\frac{1 - a}{2}\right)c^2\right]V^2 + \left[a\,(1 - a)^2 - \left(\frac{3 - 4a^2 + 3a^3}{3}\right)c + \right. \\ & \left.\left(\frac{6 - 5a + 2a^2 - 2a^3}{6}\right)c^2 - \left(\frac{1 + a - 4a^2 + 2a^3}{6}\right)c^3\right]V^3 + \ldots \end{aligned}$$

$$\begin{aligned} Y/a = {} & (1 - a)\,cV + \left[\left(\frac{2 - 3a + 2a^2}{3}\right)c - \left(\frac{1 - a}{2}\right)c^2\right]V^2 + \\ & \left[\left(\frac{3 - 6a + 7a^2 - 3a^3}{3}\right)c - \left(\frac{6 - 9a + 8a^2 - 4a^3}{6}\right)c^2 + \right. \\ & \left.\left(\frac{1 + a - 4a^2 + 2a^3}{6}\right)c^3\right]V^3 + \ldots \end{aligned}$$

Unfortunately these series do not converge rapidly when the value of V is as great as one-half so that the use of the first four terms of each series gives only an approximate value of the function represented. Moreover, the reactions do not seem to go so smoothly at 222.8° as at the higher temperatures. Nevertheless, it was possible to get some idea as to the magnitude of k_1 and k_2. The experimental data are given in Table V. It will perhaps be sufficient to state that these data lead to values of k_1 lying between 0.004 and 0.005 and a value of k_2 in the neighborhood of 0.0005. Table VI contains a summary of the results at the three higher temperatures.

TABLE V

REACTION AT 222.8°

t (corr.), min.	0	57	117	177	237	297
R	0.4864	0.4377	0.3797	0.3152	0.2825	0.2653
X	.5136	.5549	.6013	.6514	.6727	.6855
Y	.0000	.0037	.0095	.0167	.0224	.0246

TABLE VI

t, °C.	260	249.5	235.6
$k_1 \times 10^3$	37.5	18.7	8.67
$k_2 \times 10^3$	4.73	2.34	1.11

Energy of Activation.—The quantity A in the Arrhenius equation

$$\mathrm{d}\log_e k/\mathrm{d}T = A/RT^2$$

is usually interpreted as the energy of activation. This equation in integrated form is

$$A = \frac{2.303\,RT_1T_2}{T_2 - T_1}\left(\log_{10}\frac{k_{T_2}}{k_{T_1}}\right)$$

Since the ratio of k_2 to k_1 has been found to be practically constant from 235 to 260°, it follows that both reactions have the same energy of activation. From the values of k_1 at 260 and 249.5°, we find $A = 36{,}700$ calories; from the data at 260 and 235.6° we find $A = 32{,}300$ calories. The energy of activation is thus found to be about 34,000 calories.

Kinetic Mechanism of Rearrangement.—Since Reaction I is found to be of the second order with respect to R, we may suppose that when two molecules of R encounter each other under appropriate energy conditions, an activation complex is formed which, on the one hand, can break down re-forming two molecules of R and, on the other hand, can break down forming either one molecule of R and one molecule of X or two molecules of X. If the rate at which the complex breaks up forming $R + X$ (or $2X$) is not too great, the concentration of the complex will be maintained at its equilibrium value with respect to R. Under these circumstances the velocity of Reaction I will be proportional to the square of the concentration of R. Reaction I will still be one of the second order even if the complex is not in equilibrium with R but decomposes solely into $R + X$ (or $2X$), provided that the concentration, C, of the complex is always so minute that $\mathrm{d}C/\mathrm{d}t$ is negligibly small in comparison with the rate of formation of the complex or its rate of decomposition. Reaction I may then be represented by the scheme

$$2R \rightleftarrows \text{(complex)} \longrightarrow R + X \qquad \text{I(a)}$$

or

$$2R \rightleftarrows \text{(complex)} \longrightarrow 2X \qquad \text{I(b)}$$

Reaction II is a typical bimolecular process given by the scheme

$$R + \mathrm{X} \rightleftarrows \text{(complex)} \longrightarrow Y + Z \qquad \text{II}$$

Summary

1. The rearrangement of α-methoxystyrene to propiophenone is accompanied by an unusual type of side reaction in which the methoxystyrene and propiophenone react to form methane and 1,2-dibenzoylpropane.

2. The kinetics of these reactions was investigated at the temperatures, 260, 249.5, 235.6 and 222.8°.

3. Both reactions were found to be of the second order.

4. The differential equations describing the reactions were integrated in the form of infinite series.

5. The ratio of k_2 to k_1 remains virtually unchanged in the range 235–260°.

6. Both reactions have equal energies of activation, the value of which is 34,000 calories.

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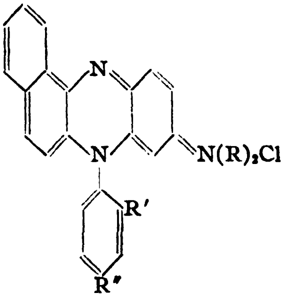
Studies on Oxidation-Reduction. XIX. Aposafranines

BY ROBERT D. STIEHLER[1] AND W. MANSFIELD CLARK

In the previous paper[2] of this series there were reported the equilibrium potentials of oxidation-reduction systems the oxidants of which are simple safranines. Data for several other azine systems, which may be designated by the names of the following oxidants, are now reported.



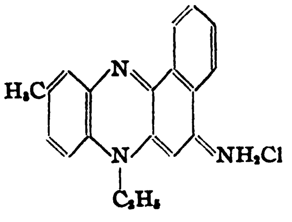
I Neutral blue (Rowe 832): $R = CH_3$; $R' = H$; $R'' = H$

II Isorosinduline No. 1: $R = C_2H_5$; $R' = H$; $R'' = H$

III Isorosinduline No. 2: $R = C_2H_5$; $R' = H$; $R'' = CH_3$

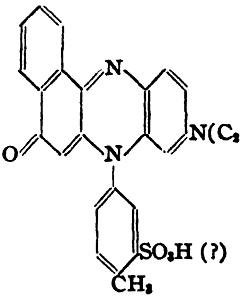
IV Isorosinduline No. 3: $R = C_2H_5$; $R' = CH_3$; $R'' = H$

V



Induline Scarlet (Rowe 827)

VI



Sulfonated Rosindone

We are indebted to Dr. H. A. Lubs and Dr. P. W. Carleton of E. I du Pont de Nemours and Company for authentic samples of all the dyes except induline scarlet

The rosindone is particularly interesting because it provided material with which to study the so-called "concentration effect" discussed in the previous paper. The results of this study support the suggestion of

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[1] R. D. Stiehler presented the details of this study in a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, The Johns Hopkins University.

[2] Stiehler, Chen and Clark, THIS JOURNAL, 55, 891 (1933).

Cohen and Preisler[3] that such a concentration effect is due to a reversible aggregation of a dye.

In the potential maesurements we encountered much the same sort of difficulties that were discussed in the previous paper. In particular it may be said that there remains an element of selection in using the minimal potentials attained after each addition of reducing agent. However, we now have to report the following significant fact. A phosphate was made with resublimed phosphorus pentoxide and potassium hydroxide prepared electrolytically by use of a mercury diaphragm. When the oxidation-reduction systems were placed in buffers made with this material, the usual reversal of potential drift was almost or entirely eliminated; the attainment of a steady potential was slower, and in all cases the amount of reducing agent used before the dye was attacked was appreciably smaller. Spectrograms failed to reveal the difference between this phosphate and the previously used phosphate, which had been prepared from recrystallized U. S. P. phosphoric acid and electrolytic sodium hydroxide. A limited series of titrations made with the "purified" buffer components and involving no reversal of potential drift gave the same constants as titrations in which minimal potentials were used.

Other aspects of electrode behavior, the special precautions, the more general methods and the standards of reference have been adequately described in previous papers.

In accordance with the scheme outlined by Clark and Cohen[4] we may derive for systems I–V the following equation relating electrode potential E_h (referred to the hydrogen standard), concentration of total reductant $[S_R]$, concentration of total oxidant $[S_O]$, hydrion activity (H^+) and apparent dissociation constants of reductant, K'_{r_1} and K'_{r_2}. E_0 is implicitly a function of the activity coefficients of the species involved and can be considered a "normal potential" only when the environment is constant.

$$E_h = E_0 - \frac{RT}{2F} \ln \frac{[S_R]}{[S_O]} + \frac{RT}{2F} \ln \left[K'_{r_1}K'_{r_2} + K'_{r_1}(H^+) + (H^+)^2\right] \qquad (1)$$

The oxidants of systems I–V possess the highly polar group $=NR_2^+$ throughout the range of *P*H considered. Therefore the dissociation constants of the oxidants may be neglected.

Equation (1) applies when no association takes place. In the case of system VI there is evidence of association of the dye in aqueous solution. This was tested by a comparison of spectrophotometric data, potentiometric measurements and the distribution coefficient for the partition of the rosindone between water and amyl alcohol.

Let it be assumed that the unimolecular species OX^- is distributed between water and amyl alcohol in accordance with:

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[3] Cohen and Preisler, Public Health Reports, Supplement 92 (1931).

[4] Clark and Cohen, *Public Health Reports*, **38**, 666 (1923).

$$\frac{[\mathrm{OX}^-]_{\mathrm{alc.}}}{[\mathrm{OX}^-]_{\mathrm{w}}} = \frac{\gamma_{\mathrm{OX}^- \text{ in w}}}{\gamma_{\mathrm{OX}^- \text{ in alc.}}} = k' \qquad (2)$$

Assuming a limited range of conditions we may replace the ratio of activity coefficients by the usual distribution coefficient, k'. The same sort of approximation is used in (3). In water let there be equilibrium between unimolecular and bimolecular forms.

$$\frac{[\mathrm{OX}^-]^2_{\mathrm{w}}}{[\mathrm{OX}_2^{--}]_{\mathrm{w}}} = K \frac{\gamma_{\mathrm{OX}_2^{--}}}{\gamma^2_{\mathrm{OX}^-}} = K' \qquad (3)$$

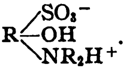
Let $C_{\mathrm{alc.}}$ and C_{w} be the total concentrations of dye in alcohol and water phases, respectively. Then

$$\frac{K'}{2} = \frac{C^2_{\mathrm{alc.}}}{(k')^2 C_{\mathrm{w}} - k' C_{\mathrm{alc}}} \qquad (4)$$

In applying this equation it will be assumed that the two solvents do not change their mutual solubilities as the concentration of the dye in each phase changes and, for the purposes of approximation, changes in activity coefficients will be neglected. We shall also neglect higher polymers the consideration of which would greatly complicate the equation.

In the case of the potentiometric measurements with the rosindone, equation (3) must be combined with the ordinary, basic equation similar to (1). There is then obtained equation (5).

$$E_{\mathrm{h}} = E_0 - \frac{RT}{2F} \ln \frac{[\mathrm{S_R}]}{[\mathrm{S_O}]} \frac{K' + \sqrt{K'^2 + 8K'[S_O]}}{2K'} + \frac{RT}{2F} \ln [K'_{r_1}K'_{r_2}(\mathrm{H}^+) + K'_{r_1}(\mathrm{H}^+)^2 + (\mathrm{H}^+)^3] \qquad (5)$$

K'_{r_1} and K'_{r_2} are the apparent dissociation constants of the phenolic and substituted ammonium groups of the reductant,  $\mathrm{R}\begin{cases}\mathrm{SO_3^-}\\ \mathrm{OH}\\ \mathrm{NR_2H^+}\end{cases}$. The sulfonic acid is assumed to be completely dissociated in solutions of oxidant and reductant. The range of experimental conditions was such that no change in the dissociation of the oxidant was observed.

Experimental

Neutral Blue (Rowe 832).—The sample was recrystallized from ethylene dibromide. The aqueous solution had a minimal transmittance at mμ = 560. Table I gives the results of a typical titration and Table II gives data sufficient to establish the relation of E_0' to P_{H} in acid solutions. Titrations in buffer solutions of P_{H} values higher than 4.2 were not satisfactory because of the very low solubility of the reductant.

Isorosindulines Nos. 1, 2 and 3.—These three dyes are very similar to neutral blue in structure and in behavior. The very limited solubility of each of the reductants precludes accurate measurements in solutions of P_{H} value greater than 4.5 or 5.0. The effects of substituents would have to be considered in connection with dissociation constants which could not be measured because of this limited solubility. Therefore it suffices to state the data of Table III which shows the slight over-all effect of substitution. The concentration effect was not studied.

TABLE I

NEUTRAL BLUE

Titration with chromous acetate. 30°. *P*H 2.946. Approximate composition of buffer: 100 ml. 1 *M* citric acid + 50 ml. 1 *M* NaOH diluted to 1 liter. Solution titrated: 75 ml. buffer + 5 ml. 0.0005 *M* dye. Reference *P*H (that of 75 ml. buffer + 5 ml. water) 2.946

y	$y - \delta$	Reduction, %	0.03006 log $[S_R]/[S_O]$	E_h corrected volt	E'_0	Deviation from average
1.0	0.5	6.84	−0.0341	0.0269	−0.0072	0.0000
2.0	1.5	20.52	− .0177	.0106	− .0071	+ .0001
3.0	2.5	34.20	− .0085	.0012	− .0073	− .0001
4.0	3.5	47.88	− .0011	− .0062	− .0073	− .0001
5.0	4.5	61.56	+ .0061	− .0133	− .0072	.0000
6.0	5.5	75.24	.0145	− .0221	(− .0076)	− .0004
7.0	6.5	88.92	.0272	− .0388	(− .0116)	− .0044
	7.31	100.00		Average	− .0072	
				By R. and B. method	− .0073	

TABLE II

NEUTRAL BLUE (ROWE 832)

Relation of E'_0 to *P*H (acid solution only) at 30°. Determined by separate titrations with chromous acetate. Total concentration of dye 3 × 10^{-5} *M*. Values used in calculations: $E_0 = +0.1697$; $K'_{r1} = 1 \times 10^{-5}$ (app.) ($pK'_{r1} = 5.0$); $E'_0 = E_0 + 0.03006 \log [K'_{r1}(H^+) + (H^+)^2]$

Buffer	*P*H	E'_0 found	E'_0 calcd.	Found−calcd.
HCl	1.072	0.1051	+0.1053	−0.0002
Citrate	2.946	− .0072	− .0072	.0000
Citrate	3.494	− .0396	− .0399	+ .0003
Acetate	4.219	− .0822	− .0820	− .0002

TABLE III

RELATION BETWEEN SYSTEMS I–IV

Values of E'_0 determined by individual titrations with chromous acetate at 30°. E_0 calculated by: $E_0 = E'_0 + 0.06011$ *P*H

	Dye	Buffer	*P*H	E_0	E_0
I	Neutral blue (Rowe 832)	Citrate	2.946	−0.0072	+0.1699
II	Isorosinduline No. 1	Citrate	3.514	− .0124	+ .1988
III	Isorosinduline No. 2	Citrate	3.509	− .0162	+ .1947
IV	Isorosinduline No. 3	Citrate	3.503	− .0090	+ .2015

Induline Scarlet (Rowe 827).—The commercial product was purified as follows. It was precipitated from hot aqueous solution by salting it out with potassium chloride. The material was then dissolved in glacial acetic acid, from which it precipitated on addition of ether. Finally, after being salted out of the aqueous solution a second and a third time with minimal quantities of potassium chloride, beautiful, clean crystals were obtained. These were washed cautiously with water.

Anal. (Kjeldahl) Calcd. for $C_{19}H_{18}N_3Cl$: N, 12.98. Found: N, 13.03, 12.82.

In dilute, aqueous acetate buffer the minimal transmittance was at mμ = 500. No concentration effect was observed by means of the spectrophotometer in concentrations as high as 1 × 10^{-3} molar.

Titrations with chromous acetate in hydrochloric acid and acid phosphate buffers were unsatisfactory because of drifting potentials. In acid citrate buffers and in neutral and alkaline buffers satisfactory data were obtained with deviations from the theoretical comparable with those of Table I. Table IV summarizes the data.

TABLE IV

INDULINE SCARLET (ROWE 827)

Relation of E_0' to P_H at 30°. Determined by separate titrations with chromous acetate. Values used in calculations $E_0 = 0.0472$. $K_r' = 3.13 \times 10^{-5}$ ($pK_r' = 4.51$) $E_0' = E_0 + 0.03006 \log [K_r'(H^+) + (H^+)^2]$. Total concentration of dye: 3×10^{-5} *M* (approx.)

Buffer	P_H	E_0' found	E_0' calculated	Found–calcd.
Citrate	2.946	−0.1300	−0.1295	−0.0005
Citrate	3.448	− .1588	− .1590	+ .0002
Acetate	4.645	− .2195	− .2197	+ .0002
Phosphate	6.488	− .2834	− .2831	− .0003
Borate	8.596	− .3465	− .3465	.0000

Sulfonated Rosindone.[5]—The dye was purified as follows. The ampholyte was precipitated from the aqueous solution of the sodium salt by cautious addition of dilute acetic acid. After a day and a half the material had become crystalline. These crystals were filtered and were repeatedly washed with large amounts of distilled water.

Anal. Calcd. for $C_{27}H_{25}O_4N_3S$: N, 8.62; S, 6.58. Calcd. for $C_{27}H_{25}O_4N_3S \cdot H_2O$: N, 8.32; S, 6.35; N/S, 3.00. Found: N, 8.37, 8.45; S, 6.39, 6.38; N/S, 3.01.

The spectrophotometric examination of this dye showed two absorption bands in water, in aqueous buffer solutions, in ethyl alcohol and in amyl alcohol. In the non-aqueous solvents the bands were narrow, the peaks sharp and there was no shift of the wave length at these peaks as the concentration of the dye was changed. In water and in aqueous buffer solutions, on the other hand, the bands were comparatively broad and both the extinction coefficients at one wave length and the wave lengths of the peaks

TABLE V

SULFONATED ROSINDONE, SPECTROPHOTOMETRIC ANALYSIS

Solvent	Concn. mole/liter	Length of soln., mm.	Band peak, mμ	Mol. extn. coeff.[a]	Band peak, mμ	Mol. extn. coeff.[a]
Ethyl alcohol	0.001	0.35[c]	518	4.3×10^4	554	5.7×10^4
	.00001	37.0	518	4.1×10^4	554	5.5×10^4
Amyl alcohol	.001[b]	0.5[c]	518	3.0×10^4	554	4.0×10^4
	.00001[b]	47.0	518	3.0×10^4	554	4.0×10^4
Aqueous borate-KCl buffer, ionic strength = 0.05	.01	0.1[c]	505	2.0×10^4	585	0.1×10^4
	.001	0.55	518	3.8×10^4	572	0.3×10^4
	.0001	5.0	524	4.0×10^4	570[d]	0.5×10^4
	.00001	45.0	527[d]	4.4×10^4	563[d]	1.4×10^4
	.000001	200.0	525[d]	3.0×10^4	562[d]	4.0×10^4

[a] Molecular extinction coefficient = $1/lm \log 1/T$ where l is length of solution in centimeters, m is concentration in mole/liter, and T is transmittance. [b] The actual concentration is slightly less than this value since the dyestuff did not dissolve completely in the original stock solution. The 0.00001 *M* solution was prepared by diluting the 0.001 *M* solution 100 fold. [c] These values may be in error since they are at the limit of the precision of the instrument. [d] These values are estimated since the absorption bands overlap.

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(5) Dr. Carleton tells us that the position of the sulfonic acid group is unknown but that it may be in the position indicated in formula VI.

varied with the concentration of the dye. In all these solvents the absorption bands changed but little with moderate alteration of the salt concentration. Table V summarizes some typical results.

These results suggest that the species present in the alcohol solutions do not change their nature with change in concentration of the dye and that in aqueous solutions such a change does occur.

To test the assumption that association occurs in aqueous solution, a series of experiments upon the distribution of the dye between two solvents was made. Amyl alcohol was the only solvent found which possesses properties satisfactory for the purpose. The results of one of the distribution experiments are given in Table VI where calculations made with equation (4) are summarized. The value of k' was determined from two sets of data in which K' could be eliminated. The agreement in the calculated values of the constant is somewhat misleading since the errors in determining the concentration of the dye in the more dilute solutions would not permit the suggested accuracy. Nevertheless the demand of equation (4) seems to have been met. Visually, the effect is striking. With very small concentrations of the dye, most of the dye is seen in the alcohol layer, while with large concentration the relation is reversed.

TABLE VI

SULFONATED ROSINDONE

Distribution of dye between amyl alcohol and water at room temperature (22° approx.).
$k' = 10$

C_{alc} mole/liter	C_{water} mole/liter	K'	C_{alc} mole/liter	C_{water} mole/liter	K'
0.0003	0.0007	2.6×10^{-6}	0.00008	0.00007	2.0×10^{-6}
.00022	.00048	2.2×10^{-6}	.000065	.000035	2.8×10^{-6}
.00018	.00032	2.2×10^{-6}	.00005	.00002	2.8×10^{-6}
.00014	.00016	2.6×10^{-6}	.00003	.000007	4.4×10^{-6}
.00011	.00009	3.0×10^{-6}	.000015	.000003	3.0×10^{-6}

A somewhat different distribution coefficient would obviously obtain were the aqueous phase a buffer solution. An experiment was made on the distribution of the dye between amyl alcohol and an aqueous solution buffered with the borate–boric acid–potassium chloride system. This gave an association constant approximately the same as that found by the potentiometric measurements with the same buffer solution.

According to equation (5), which involves the apparent polymeric dissociation constant, K', the "titration curve" relating electrode potential to percentage reduction *at constant* (H^+) should be asymmetric. This was found to be the case. However, accurate evaluations of the characteristics of the curve were difficult for the following reason.

Since an appreciable amount[6] of reducing agent, d, is used by the slight impurities of the buffer solution, it is necessary to correct y, the ml. of

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(6) Equivalent to about 2×10^{-6} normal.

reducing agent used at any given stage, by applying this "*d*-correction" before further calculations are made. Ordinarily this "*d*-correction" as well as the total amount, *A*, of reducing agent can be found by the method of Reed and Berkson.[7] In the present instance the asymmetry of the titration curve prevents the application of this method. Therefore estimates of the "*d*" and "*A*" values had to be made by a graphic method which leaves a small element of judgment.

With $[S_O]$ and the ratio $[S_R]/[S_O]$ thus established, K' could be estimated from any two sets of data. In Table VII the value of K' so estimated is rounded to 1×10^{-5}. Its application leads to a fairly satisfactory agreement in the calculated values of E'_0, the potential at 50% reduction. This is the more satisfactory when it is considered that a titration of the dye at a concentration one-tenth that recorded in Table VII gave a value of E'_0 agreeing within 0.1 millivolt. A titration of the dye at ten times the concentration recorded in Table VII gave a value of E'_0 0.9 millivolt more positive. However, the corrections are here the more uncertain and the concentration of the dye is close to saturation in borate–potassium chloride buffers.

There remains the possibility that the dye is not homogeneous, that it consists of two or more monosulfonates and that the dissymmetry of a titration curve is of an origin comparable with that found by Sullivan, Cohen and Clark[8] in their titration of *mixtures* of the sulfonates of indigo. An asymmetry of only 4 millivolts in the titration curve was found in the most dilute solution measured. If this asymmetry be ascribed entirely to a mixture of two or more monosulfonates, then their E_0 values would be at the most 4 millivolts apart. The agreement in the value of the association constant calculated from the distribution experiment and from the potentiometric measurements indicates that the greater part of the asymmetry, if not all, is due to association. Consequently if there is present a mixture of monosulfonates, they have the same, or nearly the same, E_0 values and for our purposes we can neglect the possibility of mixtures and treat the oxidant as a homogeneous compound.

Calculations with the measurements of the rosindone in phosphate buffers yielded a value of K' considerably higher than the value for borate buffers; 5×10^{-5} for phosphate buffers instead of 1×10^{-5} for borate buffers. Accordingly the calculations of Table VIII, which summarize the results, are made with these distinct constants. In this table the apparent acid dissociation constants of the reductant, K'_{r_1} and K'_{r_2} are those estimated by the usual methods (see previous papers of this series).

Part of the difference between the values for K' in the two buffers may be ascribed to a difference in ionic strengths which affect the activities.

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[7] Reed and Berkson, *J. Phys. Chem.*, **33**, 760 (1929); see also Clark and Perkins, THIS JOURNAL, **54**, 1228 (1932).

[8] Sullivan, Cohen and Clark, *Public Health Reports*, **38**, 1669 (1923).

TABLE VII

SULFONATED ROSINDONE

Titration with chromous acetate at 30°. P_H: 8.852. Approximate composition of buffer: 500 ml. 0.2 *M* boric acid + 40 ml. 1 *M* NaOH + 60 ml. 1 *M* KCl; diluted to 1 liter. Solution titrated: 50 ml. buffer + 5 ml. 0.0005 *M* dye. Reference P_H (that of 50 ml. buffer + 5 ml. water): 8.852. $K' = 1.00 \times 10^{-5}$

y ml.	$y - d$ ml.	Reduction, %	$[S_O]$ moles/liter	$0.030055 \log \frac{[S_R]}{[S_O]} \left(\frac{K' + \sqrt{K'^2 + 8K'[S_O]}}{2K'} \right)$	E_h corr	E_0	Deviation from av.
0.5	0.22	2.953	4.372×10^{-5}	−0.02928	−0.47412	(−0.50340)	−0.00017
1.0	0.72	9.66	4.033×10^{-5}	− .01331	− .48981	(− .50312)	+ .00011
1.5	1.22	16.38	3.700×10^{-5}	− .00587	− .49737	− .50324	− .00001
2.0	1.72	23.09	3.373×10^{-5}	− .00079	− .50248	− .50327	− .00004
2.5	2.22	29.80	3.052×10^{-5}	+ .00320	− .50643	− .50323	.00000
3.0	2.72	36.51	2.736×10^{-5}	.00660	− .50983	− .50323	.00000
3.5	3.22	43.22	2.427×10^{-5}	.00965	− .51289	− .50324	− .00001
4.0	3.72	49.93	2.121×10^{-5}	.01249	− .51573	− .50324	− .00001
4.5	4.22	56.65	1.822×10^{-5}	.01527	− .51849	− .50322	+ .00001
5.0	4.72	63.36	1.527×10^{-5}	.01809	− .52128	− .50319	+ .00004
5.5	5.22	70.07	1.237×10^{-5}	.02108	− .52432	− .50324	− .00001
6.0	5.72	76.78	0.952×10^{-5}	.02442	− .52780	(− .50338)	− .00015
6.5	6.22	83.49	0.671×10^{-5}	.02851	− .53210	(− .50359)	− .00036
7.0	6.72	90.20	0.395×10^{-5}	.03441	− .53859	(− .50418)	− .00095
7.5	7.22	96.91	0.124×10^{-5}	.04740	− .55158	(− .50418)	− .00095
	7.45	100.00			Average	−0.50323	

TABLE VIII

SULFONATED ROSINDONE

Relation of E_0' to P_H at 30°. Determined by separate titrations with chromous acetate. Values used in calculations: $E_0 = +0.2430$ with phosphate buffers; $+0.2513$ with borate buffers. $K' = 5 \times 10^{-6}$ with phosphate buffers; 1×10^{-6} with borate buffers. $K'_{r_1} = 3.16 \times 10^{-8}$ ($pK'_{r_1} = 7.5$). $K'_{r_2} = 3.16 \times 10^{-10}$ ($pK'_{r_2} = 9.5$). E_0 (corr.) $= E_0'$(found) $+ 0.03006 \log [K' + \sqrt{K'^2 + 8K'[\text{So}]}]/2K'$. E_0'(calcd.) $= E_0 + 0.03006 \log [K'_{r_1}K'_{r_2}(\text{H}^+) + K'_{r_1}(\text{H}^+)^2 + (\text{H}^+)^3]$

Buffer	P_H	[So] at 50% reduction	E_0' Found	E_0' Corr.	E_0' Calcd.	Corr.-calcd.
Phosphate	6.082	5.5×10^{-6}	−0.3067	−0.3045	−0.3050	+0.0005
Phosphate	6.083	15.2×10^{-6}	− .3119	− .3073	− .3050	− .0023
Phosphate	6.489	15.1×10^{-6}	− .3441	− .3395	− .3410	+ .0015
Phosphate	6.801	14.7×10^{-6}	− .3719	− .3674	− .3679	+ .0005
Phosphate	7.103	15.1×10^{-6}	− .3977	− .3931	− .3931	.0000
Phosphate	7.313	28.7×10^{-6}	− .4150	− .4082	− .4099	+ .0017
Phosphate	7.632	15.1×10^{-6}	− .4395	− .4349	− .4340	− .0009
Phosphate	7.674	21.0×10^{-6}		− .4374	− .4370	− .0004*
Phosphate	7.830	21.3×10^{-6}		− .4480	− .4480	.0000*
Phosphate	7.861	14.7×10^{-6}	− .4531	− .4486	− .4501	+ .0015
Borate	8.172	15.1×10^{-6}	− .4712	− .4603	− .4624	+ .0021
Borate	8.267	5.8×10^{-6}	− .4726	− .4658	− .4685	+ .0027
Borate	8.352	14.5×10^{-6}	− .4790	− .4682	− .4738	+ .0056
Borate	8.852	21.1×10^{-6}		− .5032	− .5032	.0000*
Borate	9.304	14.8×10^{-6}	− .5393	− .5285	− .5270	− .0015
Borate	9.467	14.9×10^{-6}	− .5461	− .5352	− .5347	− .0005
Borate	9.735	14.9×10^{-6}	− .5570	− .5461	− .5463	+ .0002
Borate	9.810	21.1×10^{-6}		− .5495	− .5494	− .0001*
Phosphate	10.689	14.9×10^{-6}	− .5911	− .5865	− .5885	+ .0020

* The starred values were calculated by equation (5) giving E_0' (corr.) directly. The other values were estimated graphically and the E_0' (Found) was then corrected for [So], consequently not as much weight was placed on these values. The error introduced by graphical estimation was not sufficient to warrant the more laborious calculations.

However, in this, as in the previous investigation, our preliminary measurements indicate that moderate variation of ionic strength causes a second order effect. We believe that the salt effect is largely specific and comparable to that noted by Sullivan, Cohen and Clark[8] in the cases of the sulfonates of indigo which behaved differently in borate and in phosphate buffers.

Since association of the dye is doubtless a first step toward the formation of a precipitable aggregate, it is important to note that our approximate measurements of the solubilities of the dye in solutions containing various buffer and neutral salts indicate that the potentiometric measurements were conducted with solutions of the dye too dilute for precipitation.

Discussion

In Fig. 1 are shown the curves relating E_0' to P_H for each of the systems studied. E_0' is the potential at 50% reduction. In the figure only the experimental data for complete titrations are shown. Less accurate supplementary data, as, for instance, those obtained by the method of mixtures, indicate that the curves are properly extrapolated, provided no resolution of the titration curve comparable to that found by Michaelis[9] in the case of rosinduline 2G in very acid solutions appears. For purposes of orientation the curves for several other systems are shown in Fig. 1. Curve 2G is for rosinduline 2G (Rowe 830), drawn according to the first data of Michaelis.[10] Rosinduline 2G has a structure very similar to VI except that it has no substituted amino group.

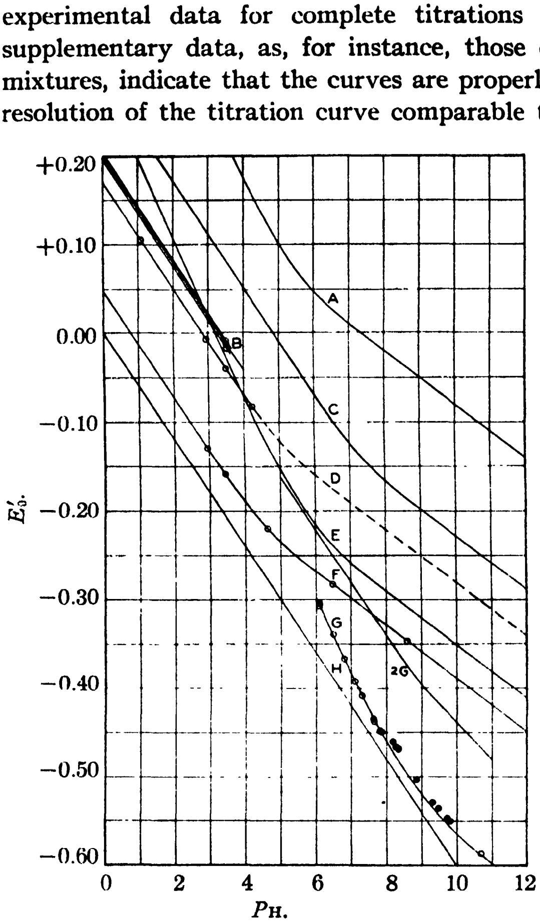

Fig. 1.—Relation of E_0' to *P*h (E_0'; potential in volts, referred to the hydrogen electrode standard, when dye is 50% reduced): A, methylene blue; B, the isorosindulines Nos. 1, 2 and 3; C, indigo disulfonate; D, neutral blue; E, dimethylphenosafranine; F, induline scarlet; G, sulfonated rosindone; O, in phosphate buffers; ●, in borate buffers; 2G, rosinduline 2G (after Michaelis); H, hydrogen electrode, 1 atm. hydrogen.

The system of induline scarlet and that of the rosindone nearly supplement one another as oxidation–reduction indicators with characteristic potentials near that of the hydrogen electrode under one atmosphere of hydrogen. In the case of the sulfonated rosindone at a concentration of total dye of 3 × $10^{-5}M$, 90% reduction, and *P*h 7.0 the potential is that of the hydrogen electrode under one atmosphere of hydrogen. We are thus encouraged to believe that these dyes will be useful in certain biochemical studies which have been delayed for lack of such indicators; but we must add the caution that in practical applications the several peculiar properties of these systems will have to be considered.

Since the reductants of the isorosindulines, I–IV, are practically insoluble in buffers of *P*h values greater than about 4.5 or 5.0, these systems

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(9) Michaelis, *J. Biol. Chem.*, **92**, 211 (1931).

(10) Michaelis, *ibid.*, **91**, 369 (1931).

are of less biochemical interest. The effects of substitution are slight but appreciable. An analysis of such effects would require knowledge of the dissociation constants.

With regard to the postulate of a reversible association of the sulfonated rosindone it may be said that there is now a first order agreement between the results of the potentiometric measurements and the results of the study of the distribution coefficient between aqueous solutions and amyl alcohol. The purely qualitative spectrophotometric data admit the same explanation. Undoubtedly the following steps of aggregation should be considered: $2O_X \rightleftharpoons O_{X_2}$; $O_X + O_{X_2} \rightleftharpoons O_{X_3}$, etc. But obviously the resulting equations would be complex and would involve too many constants for a practical test. Therefore only the first order approximation can be sought with the assumptions used. The calculations suggest that if the number of molecules in the predominant aggregate present in the alcohol is X, the numbers present in the predominant aggregates of the aqueous phase are X and $2X$, the proportion depending upon the concentration. If X were other than unity the equation involving the electrode potential would be so seriously altered that it is doubtful whether the application of equation (5) would have led to the agreement found. Therefore the "internal evidence" seems to justify the assumptions made.

In the previous paper Stiehler, Chen and Clark[2] reported several very careful titrations of safranines. Their titration curves were analyzed by the method of Reed and Berkson and failed to show the dissymmetry predicted from the evidence of aggregation found by separate titrations at different concentrations. They noted, however, that the titrations which showed no asymmetry might have been made at unsuitable concentrations.

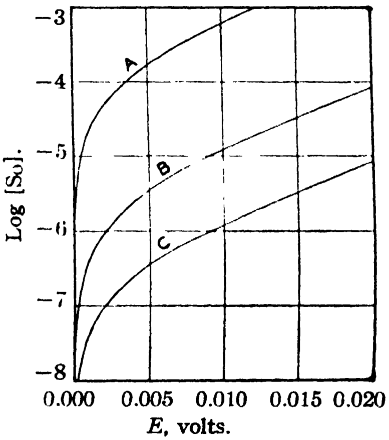

Fig. 2.—Effect of association of oxidant upon potential, K', the apparent polymeric dissociation constant: A, for $K' = 5 \times 10^{-4}$; B, for $K' = 1 \times 10^{-5}$; C, for $K' = 1 \times 10^{-6}$.

An examination of equation (5) will show that when the contribution of aggregation to the observed potential is plotted against log $[S_O]$ there is obtained a family of curves with K' as a parameter (see Fig. 2). Curve A approximately represents the case of dimethylphenosafranine.[11] If, during a titration of this dye, the value of log $[S_O]$ falls from -4.22 to -6.22, the contribution of declining association to the observed potentials should be about 2 millivolts. The resulting dissymmetry of the titration curve would escape visual inspection unless the value of the "d" correction were known. When such a curve is treated as if symmetrical by the method of Reed and Berkson, the "d" and "A" values are automatically adjusted so that the calculated values of E_0' appear constant within experimental error. In the earlier work on methylene blue[12] and on Nile blue[8] the element of judgment remained in the selection of "A" values and the slight dissymmetry of a titration curve was obscured.

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[11] See Stiehler, Chen and Clark, Ref. 2, p. 897.

Therefore the more reliable test of the "concentration effect" is that obtained when a fixed ratio of total oxidant and total reductant is used at different concentrations of the sum. Unfortunately there are limitations to the exploration of the entire course illustrated in Fig. 2. A test at dilutions great enough to bring about complete dissociation would involve measurements at concentrations of the order of millionth molar or less. This involves large experimental errors. Use of relatively high concentrations is precluded in some instances by limited solubilities and in all cases involves some uncertainty of correction for the effect of the oxidation–reduction system upon the buffer system. Therefore the empirical linear relation $\tilde{E} = E_0 + A \log C$ used in the previous paper[2] was legitimate as a first approximation applicable within narrow limits of concentration.[13] The better analysis in the case of the rosindone is made possible by the fortunate circumstance that the greatest change in association takes place within a range of concentration adapted to the potentiometric measurements (see curve B, Fig. 2).

Summary

The equilibrium potentials of six oxidation–reduction systems in which aposafranines are the oxidants have been determined at 30°.

Neutral blue (Rowe 832) and three other closely related isorosindulines have the following "normal potentials," E_0: Neutral blue, 0.170; Isorosinduline No. 1, 0.199; Isorosinduline No. 2, 0.195; Isorosinduline No. 3, 0.202. In acid solution $\Delta E_h/\Delta P_H = -0.0601$. The low solubilities of the free bases prevented measurements in neutral and alkaline solutions. A rough estimate of the dissociation constant of the neutral blue cation, treated as an acid, is 1×10^{-5}.

The system of which induline scarlet (Rowe 827) is the oxidant gave electrode potentials which may be described by the equation

$$E_h = 0.047 - 0.03006 \log [S_R]/[S_O] + 0.03006 \log [K_{r_1}'(H^+) + (H^+)^2]$$

K_{r_1}', the apparent first dissociation constant of the cation of the reductant is 3.1×10^{-5} ($pK_{r_1}' = 4.5$). At $P_H = 7.0$ and $[S_R]/[S_O] = 1$, E_h, $= -0.299$.

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(12) Clark, Cohen and Gibbs, *Public Health Reports*, **40**, 1131 (1925).

(13) The first value of $\tilde{E}_0$ in Table III of the previous communication is brought nearer to the average by the full correction.

The system of which the sulfonated rosindone is the oxidant gave electrode potentials which may be described by the equation

$$E_h = E_0 - 0.03006 \log [S_R]/[S_O] - 0.03006 \log \left[K' + \sqrt{K'^2 + 8K'[S_O]}\right]/2K' + 0.03006 \log [K'_{r_1}K'_{r_2}(H^+) + K'_{r_1}(H^+)^2 + (H^+)^3]$$

$K'_{r_1} = 3.2 \times 10^{-8}$ ($pK'_{r_1} = 7.5$); $K'_{r_2} = 3.2 \times 10^{-10}$ ($pK'_{r_2} = 9.5$). K' is the apparent dissociation constant for an equilibrium between uni- and bimolecular species. K' is approximately 5×10^{-5} when the dye is in phosphate buffers and 1×10^{-5} when the dye is in borate buffers. This specific salt effect is also reflected in the extrapolated values of E_0, 0.243 for phosphate and 0.251 for borate buffers.

Other evidences of a reversible association of the rosindone in aqueous or aqueous buffer solutions are: (1) the qualitative analysis of the changes in the spectrophotometric absorption curves which follow dilution; (2) the analysis of quantitative studies on the distribution of the dye between water and amyl alcohol. The values of K', estimated by the distribution studies, are in substantial agreement with those estimated by the potentiometric measurements.

When the sulfonated rosindone is 90% reduced, $P_H = 7.0$ (phosphate buffer) and total dye concentration is 3×10^{-5} M, the electrode potential is that of the hydrogen electrode under 1 atmosphere of hydrogen. This system gives potentials nearer that of the hydrogen electrode than any system previously reported in this series of papers on oxidation-reduction indicators.

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The Homogeneous Thermal Polymerization of Isoprene

BY WILLIAM E. VAUGHAN[1]

In an earlier publication[2] there has been reported an investigation of the homogeneous thermal polymerization of 1,3-butadiene, and in that paper there has been given a brief review of the several similar reactions hitherto studied, together with a cursory survey of some of the theoretical aspects of the general problem of association processes. There is thus no need to repeat that material. Suffice it to say that Kassel's contention[3] that the formation of polyatomic molecules by a second-order association process is possible at a relatively large fraction of all collisions, is well supported by the experimental evidence thus far presented. It may also be mentioned that the data for the three reactions considered, namely,

[1] National Research Fellow in Chemistry.

[2] Vaughan, THIS JOURNAL, 54, 3863 (1932).

[3] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., N. Y., 1932, pp. 44-47; also THIS JOURNAL, 53, 2143 (1931).

the hydrogenation of ethylene and the dimerizations of ethylene and of 1,3-butadiene, show that the ratio of the empirical second-order rate constant to that calculated from the collision frequency and the simple Maxwellian factor decreases for the reactions in the order named; this was interpreted as indicating that orientation of the properly activated particles at the moment of impact was highly important for the achievement of reaction, and that the more complex the molecules the more precise must be their mutual locations.

The present study is a continuation of the former, concerning itself with the 2-methyl derivative of 1,3-butadiene, which is known to form a dimer under certain conditions.

Experimental

The technique employed was essentially the same as that used previously. The furnace was electrically heated and its temperature manually maintained at constancy. Temperatures were determined by means of a calibrated thermometer. It is estimated that the temperature readings were accurate to ±1°. During the first several hours of all runs the variation of the temperature was within ±0.5°. The reaction cells, several of which were used, were all of 80 cc. capacity; they communicated through capillary tubing to the supply of isoprene and to a quartz spiral manometer. In those experiments where the pressure was sufficiently high so that isoprene would condense out in the tubing at the temperature of the room, the entire reaction system other than the cell, namely, the tubing and spiral manometer, was electrically heated to approximately 150°, and in such cases the reaction system was sealed off from the auxiliary trap used in conjunction with the storage vessel for the admittance of the isoprene. A mercury column served as an absolute manometer in combination with the quartz spiral which acted as a null instrument; the scale of the former was readable by means of a vernier with a precision of 0.1 mm. This figure likewise is a close estimate of the accuracy with which the fibers of the quartz spiral were adjustable.

The reactant was an Eastman Kodak Company product which was used without further chemical treatment. It was, however, fractionally distilled *in vacuo* several times, only the middle portion being preserved. In the course of the experiments two separate samples were utilized with no detectable difference in their behavior.

Data and Results

In the several runs performed observations were made of the pressures at various time intervals, chosen to correspond to approximately equal amounts of reaction. These data when plotted gave curves of the types shown in Fig. 1. The curves possessing a minimum are characteristic of all of the higher temperature experiments (above 371°), while the continuous downward trend of pressure with time shown by No. 26 of the figure is typical of rate measurements made at temperatures from 286.5 to 371°. It is these latter rates which are primarily of interest to the purposes of this study.

A number of reports[4] confirm the thermal dimerization of *liquid* isoprene,

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(4) (a) Lebedev, *J. Russ. Phys.-Chem. Soc.*, **62**, 1395 (1930); **45**, 1249 (1913); (b) Harries, *Ann.*, **383**, 206 (1911); (c) Ostromuislenski, *J. Russ. Phys.-Chem. Soc.*, **47**, 1928 (1915); (d) Aschan, *Ann.*, **439**, 221 (1924); *Ber.*, **57**, 1959 (1924); (e) Wagner-Jauregg, *ibid.*, **488**, 176 (1931); (f) Whitby and Crozier, *Canadian J. Research*, **6**, 203 (1932).

although there is some disagreement as to the nature of the dimer formed; the recent work indicates that the product is a monocyclic compound. Gapon[5] has investigated the kinetics of the polymerization of liquid isoprene at 100–150° and claims to have differentiated three second-order reactions that occur simultaneously; two dimers, dipentene and 1,3-dimethyl-1-vinylcyclohexene-3, are formed together with a complex polymer. These three processes are seemingly so clearly differentiated that he further gives as the activation energies for the three reactions, 22,400, 21,500 and 18,800 calories, respectively. In the light of the experimental difficulties involved, the precision of these results is very surprising.

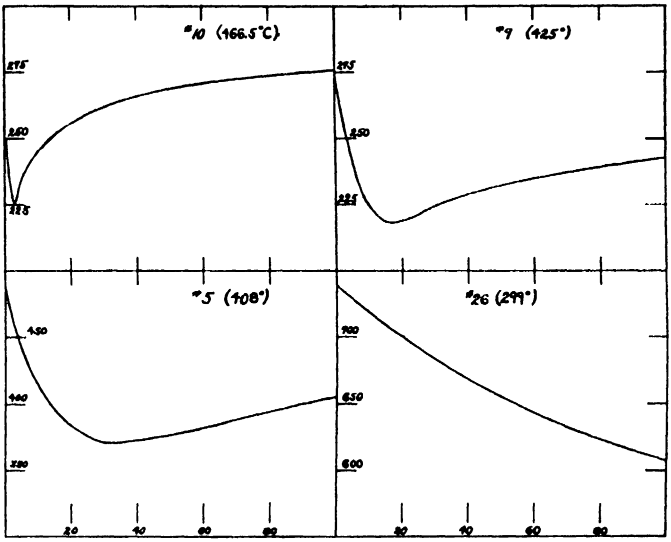

Fig. 1.—Pressure (mm.) *vs.* time (min.).

The above-mentioned results and the analogous study of butadiene obviously suggest a treatment of the pressure–time data by appplication of the integrated second-order reaction rate equation

$$k = \Delta p_I/(\Delta t)(p_{I_1})(p_{I_2}) \tag{1}$$

wherein Δp_I is the change in isoprene pressure in the interval Δt, $(t_2 - t_1)$, and p_{I_1} and p_{I_2} are the pressures of isoprene at the times t_1 and t_2. The results to which this leads are shown by Table I, which shows the rate constants, k, at various fractions of isoprene converted for Run No. 24, which was chosen as typical of the low temperature runs, and by Fig. 2, which shows a plot of such a set of data for a similar experiment.

The downward trend of k with time considered in relation to the behavior revealed in the higher temperature experiments, namely, that a pressure increase occurs after a certain pressure decrease, may be taken to indicate

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[5] Gapon, *J. Russ. Phys.-Chem. Soc.*, **62**, 1395 (1930); *J. Gen. Chem.* (U. S. S. R.), **1**, 1177 (1931).

TABLE I

RUN 24. INITIAL PRESSURE, 620.0 MM.; TEMP., 299.5°

Fraction of isoprene converted	k (mm.$^{-1}$ min.$^{-1}$) $\times 10^6$	Fraction of isoprene converted	k (mm.$^{-1}$ min.$^{-1}$) $\times 10^6$	Fraction of isoprene converted	k (mm.$^{-1}$ min.$^{-1}$) $\times 10^6$
0.080	(0.802)	0.292	0.773	0.497	0.593
.104	.834	.316	.763	.519	.589
.126	.817	.340	.738	.550	.627
.145	.834	.361	.695	.579	.569
.162	.872	.384	.699	.612	.553
.187	.861	.414	.679	.658	.488
.217	.820	.430	.624	.708	.487
.237	.824	.449	.607	.798	.418
.263	.820	.474	.603		

the presence of a subsequent decomposition of the dimer, occurring along with the formation process. Certain runs were prolonged, such as No. 5 at 408°, and it was observed that the final pressure (attained after 1080 min.) was the same as the initial pressure; it would seem, then, that one molecule of the dimer decomposes to give two molecules of gaseous products. However, in the highest temperature experiments (for example, No. 10), the final pressure exceeded the initial, indicating still further decomposition. The products of the decomposition were probably unsaturated hydrocarbons, inasmuch as freezing down with liquid air caused the pressure to drop to an unreadable amount, indicating that no hydrogen is split out. The cool cell, after the furnace was removed following the termination of a run, contained droplets of a colorless liquid condensate which had a definitely turpentine-like odor, somewhat similar to that of limonene. This material rapidly decolorized a few drops of a very dilute permanganate solution, as does limonene. In none of the lower temperature experiments was any discoloration of the cell observed but at the higher temperatures a dark film appeared on the walls.

To secure a rate constant representative of the polymerization reaction alone, undisturbed by the decomposition, the data of each run were treated as shown in Fig. 2, the constant obtained by extrapolation to zero fraction converted being taken as the true rate of the association. The construction of the straight line through the divergent points can be none too precise and the constants are certainly liable to some error. The results obtained are listed in Table II.

It may be recalled that in the case of butadiene[6] the rate constant was obtained in a similar fashion; but the extrapolation was simpler, since the constants for the intervals were invariant until 60–70% conversion was approached, at which point the constants increased, due seemingly to further polymerization, in contrast to the present steady decrease of the constants from the onset of reaction. Table II shows that in the small pressure range utilized the rate is independent of pressure

[6] See Fig. 1, p. 3867, of Ref. 2.

TABLE II

SUMMARY OF DATA

Run	Temp., °C.	Init. press., mm.	Fraction converted	*k* (mm.$^{-1}$ min.$^{-1}$ × 10^{+5})	*k* (cc. moles^{-1} sec.$^{-1}$)	Comment
11	371	223.3	0.442	14.8	93.8	
12	358	225.0	.678	7.90	51.8	
13	349	212.1	.726	5.15	33.3	
14	358	246.1	.567	6.00	41.1	Packed
15	323.5	214.2	.482	1.78	11.1	
16	323.5	424.0	.635	1.87	11.6	Packed
17	329.0	305.0	.420	2.52	15.8	
18	297.5	316.0	.453	0.79	4.68	
19	300.5	314.1	.559	.86	5.12	Hexaphenylethane
20	286.5	408.5	.527	.42	2.44	Hexaphenylethane
21	286.5	312.0	.487	.42	2.44	Hexaphenylethane; packed
22	301.0	289.4	.586	.92	5.48	Hexaphenylethane; packed
23	300.0	412.4	.726	.81	4.83	
24	299.5	620.0	.798	.93	5.53	
25	297.0	615.0	.776	.70	4.15	
26	299.0	739.0	.470	.83	4.94	

It is to be further observed that in certain of the runs, such as No. 21, shown in Fig. 2, at the beginning of the reaction there was a brief period during which there was an abrupt decrease in the values of the constants to a point where they revealed the apparent linear relationship to the fraction of isoprene converted (as was utilized in determining the rate at zero percentage conversion). It was thought that this somewhat anomalous feature might be due to an extraneous reaction such as might be

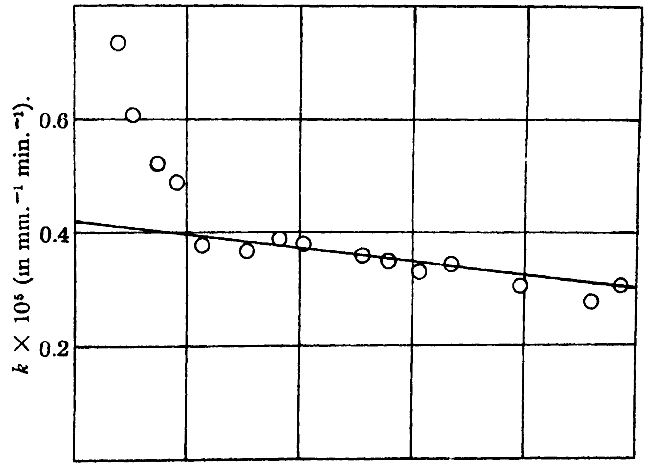

Fig. 2.—Run 21 (286.5°).

brought about by traces of peroxides in the gas, causing a catalyzed polymerization. Conant and Peterson[7] have proved in their very high pressure polymerizations of isoprene that traces of peroxides are extremely active catalysts in the process and that by treatment of the liquid reactant with hexaphenylethane the rate was reduced ten-fold. This procedure was tried in the cases of Runs 19 to 22, and this initial effect was diminished but not completely removed.

The reaction seemed to be essentially homogeneous, inasmuch as in a cell packed with lengths of Pyrex tubing so that the surface–volume ratio was increased five-fold, it proceeded with the same velocity as in the "empty" cell.

An effort was made to express quantitatively the data for the higher temperature experiments. Computation showed that in the earlier part of a given run the rate was well expressed by the simple second-order equation (1). Attempts were then made to express the total pressure over the whole range of the run as resulting from a concurrent bimolecular association and a first- or second-order decomposition of the dimer formed, but the complexity of the mathematical analysis coupled with the uncertainty of the premises led to the pigeon-holing of this phase of the problem pending further investigation.

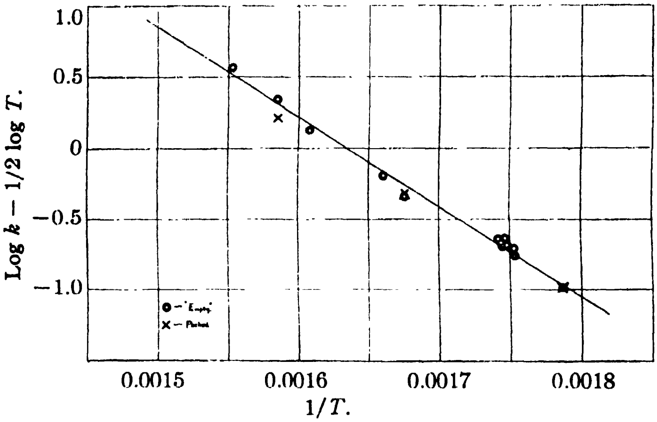

Fig. 3.

A plot of $\log_{10} k - 1/2 \log_{10} T$ *vs.* $1/T$ (k in cc. moles^{-1} sec.$^{-1}$), (in accord with the equation $k = AT^{1/2} e^{-E/RT}$), is shown in Fig. 3. The slope of the line corresponds to $E = 28{,}900$ calories and an equation expressing it is $k = 2.193(10^{10})\ T^{1/2}\ e^{-28{,}900/RT}$

Discussion of the Results

Following the method used previously[8] it is possible to determine the efficiency of molecule formation at collisions between properly activated particles. For molecules possessing in one degree of freedom an energy of 28,900 calories per mole at 570°K. the Maxwellian factor is 7.83×10^{-12}. The total number of collisions per cc. in each second is given by[9] $Z = 2N^2\sigma^2\sqrt{\pi kT/m}$, wherein N is the number of molecules of diameter σ and mass m per cc. Evaluation of Z for C_5H_8 at a concentration of one mole per liter for a temperature of 570°K. on the assumption of a diameter of 5.0×10^{-8} cm. gives 8.57×10^{31}. If molecules of the dimer resulted on each collision of properly activated molecules, the rate of disappearance of isoprene should be calculable from $2Z$ times the exponential, since two molecules react at each successful impact; this product is 2.21 (units of moles/liter and sec.). The value of the experimentally determined constant at this temperature is 4.15×10^{-3}, expressed in the same units. The ratio of these two figures is 1:530. The significance of this figure as bearing upon the orientation of the particles on collision has been treated heretofore in the discussion of the reaction mechanism for the association of polyatomic molecules.

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[7] Conant and Peterson, THIS JOURNAL, 54, 628 (1932).

[8] Ref. 2, p. 3873.

In Table III are summarized some data for the four second-order association reactions treated to date. In the last column are given the ratios which show conclusively the validity of Kassel's argument, based on theory, for the possibility of the occurrence of such processes with a reasonably high efficiency. That the ratios are not regularly decreasing with increasing complexity of the molecules involved, as might be required by the simple *a priori* picture of a "steric factor," is not unexpected, inasmuch as the "steric factor" may well be a predominating influence and yet be modified by other variables in such complex processes as the formation

TABLE III

SUMMARY OF BIMOLECULAR ASSOCIATION REACTIONS[a]

	Reaction	Ref.	Temp. range, °C.	E, cal.	k (liter. moles^{-1} secs.$^{-1}$) Theoretical	k (liter. moles^{-1} secs.$^{-1}$) Experimental	Ratio
1	$H_2 + C_2H_4 = C_2H_6$	*b*	475 -550	40,300	2.46	0.0114 (698°K.)	1/220
2	$2C_2H_4 = C_4H_8$	*c*	350 -500	35,700	0.589	.00159 (773°K.)	1/370
3	$2C_4H_6 = C_8H_{12}$	2	326 -388	25,300	273.0	.0265 (614°K.)	1/10,300
4	$2C_5H_8 = C_{10}H_{16}$	. .	286.5-371	28,900	2.21	.00415 (570°K.)	1/530

[a] In this table the data of Pease under references *b* and *c* have been recalculated in accordance with the form of the equation $E = AT^{1/2}e^{-E/RT}$; likewise a small error in the value of the average diameter of the molecule used in *b* has been adjusted.

[b] Pease, THIS JOURNAL, **54**, 1876 (1932).

[c] Pease, *ibid.*, **52**, 1158 (1930); **53**, 613 (1931).

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(9) Tolman, "Statistical Mechanics," Chemical Catalog Co., Inc., N. Y., 1927, p. 242.

of the dimer (or possibly mixture of dimers) encountered here, and that met with in the butadiene experiment.

Acknowledgment.—The author is pleased to acknowledge his indebtedness to the Gates Laboratory for the hospitality and facilities extended him, and to his associates there for aid during his stay in Pasadena.

Summary

The homogeneous thermal polymerization of isoprene has been investigated in the temperature range of 286.5 to 371° at pressures varying from 212 to 739 mm.; the principal process is interpreted as a bimolecular association reaction, the rate of which is expressible by $k = 2.19_3(10^{10}) T^{1/2}e^{-28,900/RT}$

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[CONTRIBUTION FROM THE ZOÖLOGICAL LABORATORIES, HARVARD UNIVERSITY]

Dielectric Constants: Ethanol–Diethyl Ether and Urea–Water Solutions between 0 and 50°

BY JEFFRIES WYMAN, JR.

The importance of a knowledge of the dielectric constant of the solvent as well as its change with temperature in the study of solutions is well known and requires no elaboration. The present paper is a report of routine measurements at a variety of temperatures on two sets of solvents of considerable use especially in organic and biological chemistry. The first set, consisting of mixtures of ethanol and diethyl ether, covers a range of dielectric constant from about 4 to 28. The second, comprising aqueous solutions of urea of concentrations running up to nearly 8 moles per liter, is characterized by dielectric constants greater than that of water, in fact approaching 108 at the upper limit. In this respect the urea–water solutions occupy an exceptional position and afford a convenient class of solvents of high dielectric constant. In fact, apart from certain ampholytes supposed to exist as zwitter ions and one or two compounds closely related to it, urea is the only substance known to form solutions of dielectric constant greater than that of water.[1] Existing data on the dielectric constant of both the above sets of liquids are somewhat incomplete and contain inconsistencies. The present results serve to extend the list of mixed solvents of accurately known dielectric properties such as those dealt with in recent papers by Åkerlöf[2] and Wyman.[3]

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(1) See Devoto, *Gazz. chim. ital.*, 61, 897 (1932); also Wyman and McMeekin, THIS JOURNAL, 55, 908 (1933); 55, 915 (1933).

(2) Åkerlöf, *ibid.*, 54, 4125 (1932).

(3) Wyman, *ibid.*, 53, 3292 (1931).

The values given in the present investigation were obtained by an absolute method, were reproducible to better than 0.1%, and, it is believed, are entirely free from systematic errors. The principle underlying this method consists in determining the electrical resonance point of a small metal circuit completely immersed in the dielectric to be measured. The dielectric constant in question is equal to the square of the ratio of this resonant wave length divided by the resonant wave length of the same circuit in a vacuum, or, in practice, in air.[4] The size of the resonant circuit required for use at a given wave length increases rapidly with decrease in the dielectric constant. In the case of the alcohol–ether mixtures the circuit required for use at convenient wave lengths is considerable and would ordinarily involve more than a liter of liquid for adequate immersion to include the entire field. For this reason a special type of resonator built up of concentric cylinders and having a very small stray field was employed. This circuit necessitated the use of less than 100 cc. of solution for satisfactory immersion and at 25° resonated at 8.612 meters in pure ether and at 20.69 meters in pure alcohol. A description of this form of resonator has been given elsewhere.[5]

In order to make sure that no systematic errors were introduced by the use of such small amounts of liquid, owing to the stray field of the resonator not included in the liquid, a careful comparison was made of the dielectric constant of a sample of alcohol at 25° determined in one case with the resonator immersed in a large volume of liquid and in the other case with the resonator in a small tight-fitting glass vessel containing about 75 cc. and jacketed with circulating water drawn from the thermostat. The two values obtained for the dielectric constant were 24.32 and 24.33, respectively, the difference being no greater than the experimental error of the determinations.

In the case of the urea–water solutions, owing to the much greater values of the dielectric constant, it was convenient to use a small spiral resonator having a resonant wave length of 0.4111 meter in air. Although this resonator had a relatively far larger stray field than the other it was so small that it could be used with about 120 cc. of solution in a double-walled Pyrex vessel jacketed with circulating water of the desired temperature.

In the case of all the solutions investigated the variation of dielectric constant with temperature can be expressed with an accuracy as great as that of the measurements by means of the second degree equation: $\epsilon = a - b(t - 25) + c(t - 25)^2$. In this equation ϵ denotes the dielectric constant at temperature t, a is the dielectric constant at 25°, and b and c are constants. The experimental results which follow are therefore presented in terms of these constants.

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(4) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(5) Wyman and McMeekin, THIS JOURNAL, **55**, 915 (1933).

II. Alcohol–Ether Mixtures.—These solutions were made up gravimetrically from the best commercial materials. The density of the alcohol, determined with a pycnometer, was found to be 0.7853 as compared with the figure 0.7851 given by "International Critical Tables." The discrepancy would correspond to less than 0.07% H_2O, which would make a difference of about 0.03 in the dielectric constant, an amount not greater than the errors of the measurement. In the case of the ether, owing to the high vapor pressure, it was not practicable to determine the density so accurately. The figure obtained, 0.708, is to be compared with the value 0.7077 from "International Critical Tables." It seemed unwise to attempt further purification of the sodium distilled ether from a sealed metal container on which the measurements are based. The results are contained in Table I.

TABLE I

DIELECTRIC CONSTANT OF MIXTURES OF ETHANOL AND ETHER IN TERMS OF THE EQUATION: $\epsilon = a - b(t - 25) + c(t - 25)^2$

Ethanol, weight per cent.	ρ (25°)	a	b	$c \times 10^4$
0	0.708	4.235	0 0198	5
13.08	.722	5.885	.0323	18
20.86	.728	6.998	0409	24
30.82	.737	8.712	.0540	31
41.24	.745	10.76	.0694	38
51.47	752	12.89	0858	42
61.93	.7614	15.26	.1018	45
70.05[a]	.7677	17.20	.1145	45
77.40	.7708	18.90	.1246	44
86 20	.7766	20.96	.1369	41
100.00	.7853	24.28	1570	20

[a] Composition based on dielectric constant at 20°.

Urea Solutions.—The urea solutions were made up gravimetrically from Merck C. P. product and the density of each determined at 25° with a pycnometer. It was found that solutions allowed to stand for several hours at a temperature above 30 or 35° underwent a change associated with an increase of conductivity. For this reason measurements at lower temperatures were made first and the work above 25° was carried out as quickly as possible before the conductivity had shown any considerable increase, and before the dielectric constant showed any change independent of temperature. A similar change in the dielectric properties of urea solutions after standing for several days has been reported by Walden and Werner,[6] and Kockel[7] states that above 35° urea undergoes an irreversible change. The results are given in Table II and shown graphically in Fig. 1, where the full lines correspond to the values of *a*, *b* and *c* given in Table II and the circles are the experimental points. The accuracy of these data is not so great as in the case of the alcohol–ether mixtures owing to the far greater

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(6) Walden and Werner, *Z. physik. Chem.*, **129**, 405 (1927).

(7) Kockel, *Ann. Physik*, **77**, 417 (1925).

TABLE II

DIELECTRIC CONSTANT OF UREA–WATER MIXTURES IN TERMS OF THE EQUATION: $\epsilon = a - b(t - 25) + c(t - 25)^2$

Weight per cent. of urea	ρ 25°	Moles/liter (25°)	a	b	$c \times 10^5$
0	0.9971	0	78.54	0.362	70
11.52	1.0284	1.973	83.90	.376	75
20.31	1.0524	3.559	87.95	.385	81
29.64	1.0788	5.325	91.76	.391	85
36.83	1.0994	6.743	94.43	.394	89
42.47	1.1159	7.892	96.58	.397	92

conductivities which reduce the sharpness of the resonance settings. The conductivity of a 2.5 molar solution at 25° was about 37×10^{-6} ohms^{-1}.

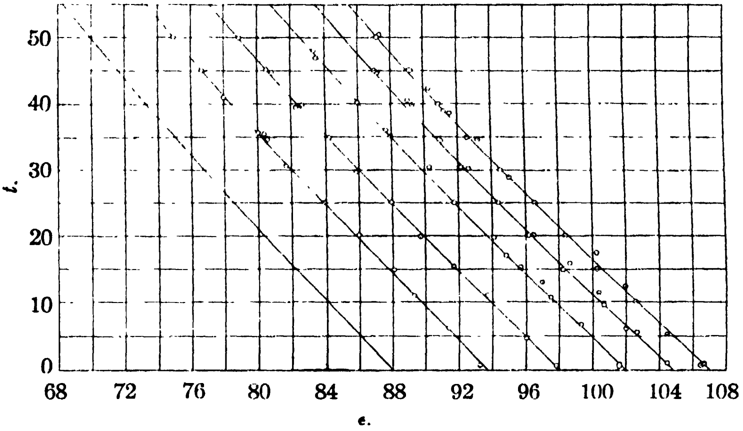

Fig. 1.

IV.—The data given in section II on the ethanol–ether mixtures may be compared with the results of other investigators. In the case of earlier

TABLE III

VALUES REPORTED FOR THE DIELECTRIC CONSTANT OF ETHER

Observer	Temperature, °C.	Dielectric constant
Richards and Shipley[8]	20	4.355
King and Patrick[9]	20	4.35
Grimm and Patrick[10]	34.5	4 11
Meyer[11]	16.6	4.3446
Scheremetzinskaja[12]	20	4.811
Estermann[13]	20	4.276
Matsouike[14]	25	4.362

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(8) T. W. Richards and J. W. Shipley, THIS JOURNAL, **41**, 2002 (1919).

(9) King and Patrick, *ibid.*, **43**, 1835 (1921).

(10) Grimm and Patrick, *ibid.*, **45**, 2794 (1923).

(11) E. H. L. Meyer, *Ann. Physik*, **75**, 801 (1924).

(12) S. Scheremetzinskaja, *J. Russ. Phys.-Chem. Soc., Phys. Teil.*, **59**, 499 (1927).

(13) Estermann, *Z. physik. Chem.*, **B1**, 134 (1928).

(14) Matsouike, *Proc. Imp. Acad. Tokyo*, **5**, 29 (1929).

data on pure ether, there is considerable disagreement, as shown by Table III. The author's value of 4.336 at 20° is in best agreement with the figures of Richards and Shipley and of King and Patrick. The latter observers also report the dielectric constant of mixtures of ethanol and ether of 10, 20, 30, 100% by weight at 20°. Their values, which are given only to either two or three significant figures, are 1 or 2% higher than those reported above.

As regards the urea solutions there is a considerable discrepancy between the measurements at a single temperature by Harrington,[15] Furth[16] Walden and Werner,[6] Kniekamp[17] and Devoto,[18] none of which were extended to a concentration greater than about 3 moles per liter. The present results, on the basis of the limiting value of the dielectric constant–concentration curve at zero concentration, agree best with the values of Walden and Werner.[6]

Kockel[7] has carried out an investigation of the effect of temperature on the dielectric constant of urea solutions of 5, 10 and 15% by weight. These results have been applied by Lange and Robinson[19] to their data on the integral heats of dilution of potassium chloride in 5% urea solutions on the basis of the theory of Debye. Lange and Robinson point out that in accordance with an extension of the original theory the limiting slope of the curve relating the heat to the square root of the molar concentration should be given approximately by the expression

$$\frac{-1.66116 \times 10^7}{\epsilon} \times \frac{1}{\sqrt{\epsilon T}}\left(1 + \frac{T}{\epsilon}\frac{d\epsilon}{dT}\right) = A$$

where ϵ is the dielectric constant of the solvent and T is the absolute temperature. In terms of Kockel's data this expression actually demands a negative heat of dilution ($A = -228$) for potassium chloride in 5% urea. This is quite at variance with the facts, which show that the heats in this solvent are positive (A observed $= 332$) and only slightly lower than those in water and in a 15% sugar solution, for which the theoretical values of A are given as 661 and 532 and the observed values as 376 and 386, respectively. On the basis of the data presented in this paper the value of A calculated from the above expression for the 5% urea solution is 440, which is in as good agreement with the facts as in either of the other cases. It may be noted that the theoretical values of A for water as well as the 15% sugar solution given by Lange and Robinson are also based on the data of Kockel. If Wyman's[4] data for water, used elsewhere by Lange, are substituted, the value obtained for A is 513.

(15) Harrington, *Phys. Rev.*, **8**, 581 (1916).

(16) Furth, *Ann. Physik*, **70**, 163 (1923).

(17) Kniekamp, *Z. Physik*, **51**, 95 (1928).

(18) Devoto, *Gazz. chim. ital.*, **60**, 520 (1930).

(19) Lange and Robinson, THIS JOURNAL, **52**, 4218 (1930). The author's attention was called to these results by Professor George Scatchard.

Summary

A report is given of a study of the variation with temperature, between 0 and 50°, of the dielectric constant of ethanol–diethyl ether and urea–water solutions as determined by a resonance method at wave lengths between 3.6 and 20 meters. The results are compared with data of previous investigators, and, in the case of the urea–water solutions, are applied to studies of Lange and Robinson on heats of dilution.

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[CONTRIBUTION FROM THE WALKER LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE]

The Binary System Lead Iodide–Potassium Iodide[1]

BY HENRY S. VAN KLOOSTER AND EDWIN I. STEARNS

The melting point of lead iodide has been reported at such variant temperatures as 358[2] and 412°.[3] The melting point of potassium iodide has been given as low as 634° (1878)[4] and as high as 723°.[5] Many workers have confirmed the fact that only the double salt $KPbI_3 \cdot 2H_2O$ exists in the ternary system PbI_2–KI–H_2O,[6,7] but the anhydrous binary system has not heretofore been examined.

C. H. Herty[8] has driven off the water from this hydrate, $KPbI_3 \cdot 2H_2O$, and states that at 310° the salt decomposes with the liberation of iodine. It was therefore the purpose of this work to find the melting points of these two iodides and to decide what anhydrous double salts they form by determining the phase diagram by means of cooling curves.

The difficulty in melting lead iodide is that it decomposes in the presence of air. Several oxyiodides have been reported[9] but they have not been examined in the light of the phase rule and are thus to be considered on probation.

Apparatus and Materials.—The tube used to melt the various mixtures consisted, as illustrated in Fig. 1, of an outer test-tube and an inner air-excluding and thermocouple-protecting tube. This inner tube excluded the air by three factors. Its volume expelled nearly all the air to begin with, and further access of air was hindered both by the snugness with which the two tubes fit together and by the bulge of the inner tube resting upon the rim of the outer. The amount of decomposition could be seen by the iodine that condensed on the upper part of the tube which protruded from the furnace. A cooling curve taken when nitrogen filled the space between the inner and outer tubes, in which case no decomposition occurred, could not be distinguished from a cooling curve taken with the inner tube as the sole protection, in which case a small ring of iodine was formed.

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[1] A thesis presented in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of Arts and Science of Rensselaer Polytechnic Institute.

[2] F. Matthes and K. Monkemeyer, *Neues Jahrb. B. B.*, **22**, i (1906).

[3] German and Metz, *J. Phys. Chem.*, **35**, 1944 (1931).

[4] "Phys.-Chem. Tabellen," Landolt und Börnstein, 1894.

[5] J. McCrae, *Wied. Ann.*, **55**, 95 (1895).

[6] N. Demassieux, *Compt. rend.*, **177**, 51 (1923).

[7] L. J. Burrage, *J. Chem. Soc.*, **129**, 1703 (1926).

[8] Herty, *Amer. Chem. J.*, **18**, 292 (1896).

[9] Mellor, "Treatise," Vol. VII, p. 766.

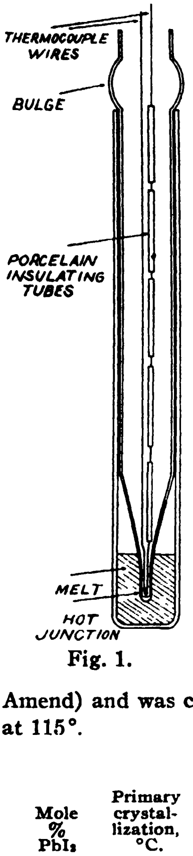

Fig. 1.

The thermocouple was of nichrome and alumel and the cold junction was kept at 20°. It was carefully calibrated with pure cadmium, lead, zinc and antimony. The calibration curve was very nearly a straight line and was extended as a straight line to beyond the melting point of potassium iodide.

An electric furnace was the source of heat and the e. m. f. was read with a millivolt meter made by Chas. Engelhard.

The lead iodide used in determining the equilibrium diagram was commercial lead iodide. Its purity is indicated by its cooling curve which has a long and strong horizontal and by the fact that its melting point, 412°, coincides with the melting point of C. P. lead iodide. The C. P. lead iodide was made by the admixture of solutions of C. P. lead nitrate (J. T. Baker Co.) and C. P. potassium iodide (J. T. Baker Co.) in the correct molar proportions. The precipitated lead iodide was washed by decantation ten times until a saturated ferrous sulfate solution placed above a 1 to 1 mixture of wash water and sulfuric acid no longer showed a brown color. It was then decanted five times more, placed on a filter, and washed ten times, allowing the previous water to drain off completely before adding more. It was then dried in an oven at 115° for two hours, pulverized, and further dried at 115° for three hours.

The potassium iodide was of U. S. P. quality (Eimer and Amend) and was crystallized twice from pure water. It was then dried for six hours at 115°.

EXPERIMENTAL RESULTS

Mole % PbI_2	Primary crystallization, °C.	Eutectic, °C.	Mole % PbI_2	Primary crystallization, °C.	Eutectic, °C.	Mole % PbI_2	Primary crystallization, °C.	Eutectic, °C
100	412	...	65	330	321	30	504	346
95	404	321	60	337	321	25	548	346
90	395	321	55	345	321	20	585	346
85	383	321	50	349	...	15	609	347
80	367	321	47.5	...	346	10	641	...
75	349	321	45	378	346	5	660	...
70	324	321	40	422	346	0	686	...
69	...	321	35	475	346			

Discussion of Results.—The phase diagram (Fig. 2) is a common type in which the two components form a congruently melting compound. It shows definitely that the compound $KPbI_3$ is the only anhydrous double salt formed. The melting point found for lead iodide, 412 ± 1°, is in exact agreement with the work of German and Metz previously referred to. It is thus recommended that this value be accepted as the true melting point. The melting point of potassium iodide, 686 ± 1°, is reasonably close to the value 684° given by Rassow[10] but does not check exactly with any given in the literature. The 346° eutectic composition is exceptionally close to the compound composition, but this is to be expected from the great difference in the melting points of $KPbI_3$ and KI.

The method of locating eutectic composition by plotting the eutectic halts against the composition of the melts and choosing the maximum was only approximate here, because unequal weights of samples were used and unequal rates of cooling prevailed. However, the eutectic compositions could be quite satisfactorily found by the intersection of the lines drawn through the points of primary crystallization.

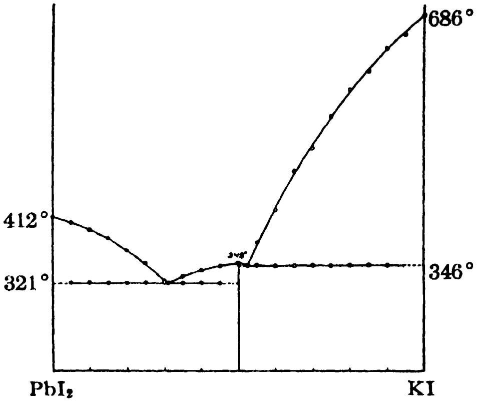

Fig. 2.—Phase diagram of PbI_2–KI.

Summary

The phase diagram of the binary system PbI_2–KI has been determined. Significant points are the three melting points, PbI_2 at 412°, $KPbI_3$ at 349°, KI at 686° and two eutectics, 69 mole % PbI_2 at 321°, and $47^1/_2$ mole % PbI_2 at 346°.

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[10] Rassow, *Z. anorg. allgem. Chem.*, **114**, 117 (1920).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions as a Function of the Concentration. II. Potassium Bromide and Potassium Chloride

BY GRINNELL JONES AND SAMUEL K. TALLEY

Recent papers from this Laboratory[1] have pointed out the significance of viscosities in the development of the modern theory of electrolytic solutions and have recorded data obtained by an improved technique. The present paper contains new data on aqueous solutions of potassium bromide over a wide range of concentration (0.001 to 3.75 *N*) and an extension of the data already published for potassium chloride up to 3 *N*.

Our new method of timing by means of a photoelectric cell which has been described in detail in the third paper referred to was used. The salts were carefully purified and are believed to have contained no impurities in significant amounts. The data are recorded in Table I in which the headings have the same significance as in our earlier paper, except that instead of giving the absolute densities of the solutions, the relative apparent densities in air (*i. e.*, the weight of the solution divided by the weight of an equal volume of water at the same temperature with no vacuum corrections applied) are given because this is the figure needed for the present

TABLE I

RELATIVE VISCOSITY AT 25°

c	d_c/d_0	t_c	t_0	d_ct_c/d_0t_0	K. E. corr.	η obs.	η comp.	$\Delta\eta$ obs. − comp.
Potassium Bromide								
0.001000	1.000089	618.55	618.54	1.00010	0.00000	1.00010	1.00010	0.00000
.002000	1.000160	618.60	618.64	1.00010	.00000	1.00010	1.00011	− .00001
.005000	1.000417	618.39	618.59	1.00009	.00000	1.00009	1.00009	.00000
.010005	1.000841	618.26	618.79	0.99998	.00000	0.99998	0.99998	+ .00000
.020001	1.001695	617.51	618.72	.99974	− .00002	.99972	.99969	+ .00003
.050001	1.004256	615.12	618.49	.99879	− .00005	.99874	.99864	+ .00010
.099899	1.008492	611.34	618.46	.99688	− .00010	.99678	.99672	+ .00006
.199882	1.016955	603.98	618.50	.99308	− .00021	.99287	.99281	+ .00006
.499927	1.042194	582.87	618.38	.98235	− .00055	.98180	.98189	− .00009
.959172	1.080449	555.29	618.59	.96989	− .00104	.96885	.96884	+ .00001
.998357	1.083718	553.06	618.50	.96906	− .00108	.96798	.96795	+ .00003
1.999826	1.166031	509.04	618.63	.95959	− .00203	.95756	.95747	+ .00009
2.003090	1.166167	508.96	618.53	.95947	− .00203	.95744	.95747	− .00003
3.030933	1.249592	481.41	618.68	.97234	− .00281	.96953	.97181	− .00228
3.749274	1.307264	470.81	618.58	.99498	− .00321	.99177	.99695	− .00518
Potassium Chloride								
0.498450	1.023223	603.23	618.58	0.99783	−0.00023	0.99760	0.99764	−0.00004
.999718	1.045948	589.99	618.67	.99746	− .00044	.99702	.99716	− .00014
2.011510	1.090591	572.19	618.77	1.00849	− .00076	1.00773	1.00765	+ .00008
2.962076	1.131272	565.65	619.45	1.03302	− .00091	1.03211	1.03221	− .00010

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(1) Grinnell Jones and Malcolm Dole, THIS JOURNAL, 51, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, 55, 624 (1933); Grinnell Jones and S. K. Talley, *Physics*, 4, 218 (1933).

purpose. For the dilute solutions reported in the earlier paper the difference is insignificant. All measurements were made at 25.00°.

It will be noted that although all solutions of potassium bromide within the range of 0.01 to 3.75 normal have a viscosity less than that of water, nevertheless the 0.001, 0.002 and 0.005 normal solutions have a viscosity greater than that of water. This furnishes another case supporting the prediction of Jones and Dole that "At very low concentrations the viscosities of solutions of all strong electrolytes will be greater than that of water, including salts which at moderate concentrations show diminished viscosity."

The data recorded in this paper show that an equation of the form $\eta = 1 + A\sqrt{c} - Bc$, is only valid up to about 0.1 N for solutions of potassium bromide and up to about 0.2 N for solutions of potassium chloride. Both of these salts have a minimum viscosity (at about 0.8 normal for potassium chloride and at about 1.9 normal for potassium bromide). Other data in the literature indicate that salts which give solutions having a viscosity less than that of water will commonly have a minimum in their viscosity–concentration curves and again have a viscosity greater than that of water at high concentrations if they are sufficiently soluble. A more detailed discussion of the laws for the viscosity of concentrated solutions will be postponed until more extensive data are available. The results so far obtained, however, indicate that another term proportional to the square of the concentration must be added.

The viscosity of solutions of potassium bromide up to 2 N can be expressed approximately by the equation

$$\eta = 1 + 0.00474\sqrt{c} - 0.04904\,c + 0.01221\,c^2$$

The values computed by this equation are given in the table in the next to the last column. The greatest deviation up to 2 N is only 0.01%. The value of the coefficient of the square root term computed from the formula of Falkenhagen and Vernon[2] is 0.0049 which agrees satisfactorily with the value 0.00474 obtained from our experiments. For potassium chloride the equation

$$\eta = 1 + 0.0052\sqrt{c} - 0.01612\,c + 0.00808\,c^2$$

holds approximately up to 3 N. The greatest deviation between our experimental data and the values computed by this equation is only 0.016%.

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(2) H. Falkenhagen, *Physik. Z.*, 32, 365, 745 (1931); H. Falkenhagen and E. L. Vernon, *ibid.*, 33, 140 (1932); *Phil. Mag.*, [7] 14, 537 (1932); L. Onsager and R. M. Fuoss, *J. Phys. Chem.* 36, 2689 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Electron Diffraction and Molecular Structure: Carbonyl Compounds[1]

BY RALPH W. DORNTE[2]

This investigation was undertaken to determine the effect of the oxygen double bond on the valence angles of the carbon atom. Previous work[3] has shown that the angle between the halogen atoms of disubstituted methanes is 125° and becomes 115° in the case of the trisubstituted methanes. It seems desirable, therefore, to study this effect in carbonyl compounds and to determine their molecular structures.

The angular intensity of electrons diffracted by gas molecules with random orientation may be calculated by the equation[4]

$$I = k\ \Sigma_i\Sigma_j\psi_i\psi_j \frac{\sin x_{ij}}{x_{ij}} \qquad (1)$$

in which

$$x_{ij} = 4\pi l_{ij} \sin \Theta/2/\lambda \qquad (1a)$$

I is the relative intensity of electrons scattered at the angle Θ, k is a constant under the experimental conditions, the ψ's are the electron scattering coefficients of the atoms, l_{ij} is the distance between the ith and jth atoms of the molecule and λ is the wave length of the electrons. The double summation extends over all atoms of the molecule considered. The self-consistency of Wierl's results[5] and their agreement with x-ray diffraction data have shown that Z, the atomic number of the atom, may be substituted for ψ in Eq. 1 rather than the expression derived by Mott.[6] This simplified calculation of the theoretical intensity curves has been employed in the present work.

Experimental Procedure.—The procedure for electron diffraction is to allow a narrow beam of electrons to intersect a gas stream and to register the diffracted electrons on a photographic plate. The apparatus followed essentially the design by Wierl.[7] A hydrogen discharge served as a source of electrons which were accelerated by constant potential D. C.[8] The accelerating potential was measured by a calibrated electrostatic voltmeter. The electrons entered the diffraction chamber through a circular slit (0.1 mm.) in the electron nozzle which was at right angles to the gas nozzle. A trap immediately above the gas nozzle condensed the gas entering the diffraction chamber, which was evacuated by a high speed diffusion pump.[9] A mechanical shutter interrupting the electron beam controlled the time of exposure. The diffraction photographs were photometered with a Zeiss recording microphotometer; the diameters of the diffraction rings were measured on the enlarged photometer curves. This procedure avoided the physiological error inherent in measurements on the diffraction picture.

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(1) Presented at the Chicago Meeting of the American Chemical Society, September, 1933.

(2) National Research Fellow in Chemistry.

(3) L. Bewilogua, *Physik. Z.*, **32**, 265 (1931); R. W. Dornte, *J. Chem. Phys.*, **1**, 630 (1933).

(4) P. Debye, *Ann. Physik*, **46**, 809 (1915); H. Mark and R. Wierl, *Fortschr. Chem., Physik physik. Chem.*, **B21**, 4 (1931).

(5) R. Wierl, *Ann. Physik*, [5] **13**, 453 (1932).

(6) N. F. Mott, *Proc. Roy. Soc.* (London), **A127**, 658 (1930).

(7) R. Wierl, *Ann. Physik*, [5] **8**, 521 (1931).

(8) A. W. Hull, *Gen. Elec. Rev.*, **19**, 193 (1916).

Preparation of Materials.—Carbonyl sulfide was obtained by dropping 50% sulfuric acid on potassium thiocyanate. The gas was purified by passage through a concentrated solution of potassium hydroxide, concentrated sulfuric acid, calcium chloride and charcoal. The product was condensed and fractionated.

The carbonyl chloride was a Kahlbaum product which was dried over phosphorus pentoxide and fractionated.

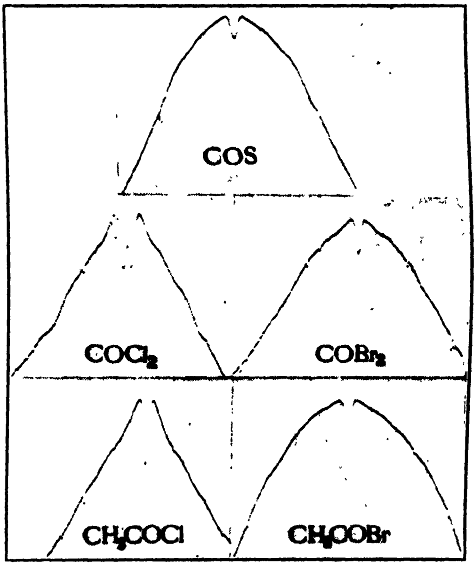

Fig. 1.—Microphotometer curves of electron diffraction photographs.

Carbonyl bromide was prepared by the action of concentrated sulfuric acid on carbon tetrabromide and purified by shaking with mercury and fractionation.

The acetyl chloride and bromide were obtained from the Eastman Kodak Company and were fractionated.

Results and Discussion

The photographs were obtained with electrons having a wave length corresponding to 45 kv. Figure 1 shows typical microphotometer curves of the diffraction pictures. The abscissas of these curves have been enlarged two-fold to emphasize the "bumps" indicating the diffraction maxima. In Table I are recorded, (1) the x values of the diffraction maxima, calculated for a definite molecular model, (2) the experimentally determined values of $\sin \Theta/2/\lambda$ for each maximum and (3) l, the corresponding carbon–oxygen interatomic distance in Å.

For carbonyl sulfide the relative intensity equation becomes

$$\frac{I}{k} = 2Z_CZ_O\frac{\sin x}{x} + 2Z_CZ_S\frac{\sin 1.40\,x}{1.40\,x} + 2Z_OZ_S\frac{\sin 2.40\,x}{2.40\,x} + Z_C^2 + Z_O^2 + Z_S^2 \qquad (2)$$

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(9) I. Estermann and H. T. Byck, *Rev. Sci. Inst.*, **3**, 482 (1932).

TABLE I

Carbonyl Sulfide

	(Sin θ/2)/λ	l(C–O in Å.)
5.85	0.412	1.13
8.60	.604	1.13
10.75	.759	1.13

C–S = 1.58 ± 0.08 Å.
C–O = 1.13 ± 0.05

Carbonyl Chloride

3.10	0.221	1.11
5.40	.385	1.12
8.05	.588	1.09
12.40	.854	1.14

C–O = 1.12 ± 0.02 Å.
C–Cl = 1.80 ± 0.04
Cl–O = 2.62 ± 0.05
<Cl–C–Cl = 110° ± 5°

Carbonyl Bromide

2.70	0.191	1.12
4.80	.341	1.12
7.15	.503	1.13
8.70	.610	1.13
11.05	.776	1.13

C–O = 1.13 ± 0.02 Å.
C–Br = 2.05 ± 0.04
Br–O = 2.85 ± 0.06
<Br–C–Br = 110° ± 5°

Acetyl Chloride

	(Sin θ/2)/λ	l(C–O in Å.)
3.30	0.232	1.13
5.80	.400	1.15
8.55	.597	1.14
11.50	.794	1.15

C–O = 1.14 ± 0.05 Å.
C–C = 1.54 ± 0.08
C–Cl = 1.82 ± 0.10
<C–C–Cl = 110° ± 10°

Acetyl Bromide

3.15	0.217	1.15
5.30	.376	1.12
7.75	.547	1.13
10.50	.742	1.12
12.80	.903	1.13

C–O = 1.13 ± 0.05 Å.
C–C = 1.54 ± 0.08
C–Br = 2.06 ± 0.10
<C–C–Br = 110° ± 10°

Equation 2 has been found to give the best correlation of the calculated and observed maxima, and is based on a linear model with C–O = 1.13 and C–S = 1.58 Å. A linear structure is consistent with the rather small electric moment of carbonyl sulfide.(10) The crystal structure of solid carbonyl sulfide has been determined by Vegard,(11) who found a linear structure with C–O = 1.10 and C–S = 1.96 Å. Dadieu and Kohlrausch(12) determined the interatomic distances, C–O = 1.04 and C–S = 2.38 Å., from the Raman effect and previous results on the infra-red absorption spectrum.(13) The nuclear separations obtained in this investigation are in good agreement with Wierl's results for carbon dioxide and carbon disulfide(7) and with the values C≡O = 1.13 and C═S = 1.63 Å. which are derived from the atomic radii formulated by Pauling.(14) It seems probable that the discrepancy among the several values for the interatomic distances of carbonyl sulfide may arise from resonance between two or more Lewis structures of the molecule as in the case of nitrous oxide.[15] For phosgene Eq. 1 becomes

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(10) C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, Appendix 1.

(11) L. Vegard, *Z. Krist.*, **77**, 411 (1931).

(12) A. Dadieu and K. W. F. Kohlrausch, *Physik. Z.*, **33**, 165 (1932).

(13) C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc.* (London), **A135**, 375 (1932).

(14) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

$$\frac{I}{k} = 2Z_CZ_O\frac{\sin x}{x} + 4Z_CZ_{Cl}\frac{\sin 1.61\,x}{1.61\,x} + 4Z_OZ_{Cl}\frac{\sin 2.34\,x}{2.34\,x} + 2Z_{Cl}^2\left(1 + \frac{\sin 2.64\,x}{2.64\,x}\right) + Z_C^2 + Z_O^2 \qquad (3)$$

This intensity equation is based on a plane "Y" model with a 110° angle between the carbon–chlorine bonds. Intensity curves were calculated with this angle taking values from 100 to 135°, but the best correlation of calculated and observed maxima was obtained at 110°. The intensity distribution for carbonyl bromide is

$$\frac{I}{k} = 2Z_CZ_O\frac{\sin x}{x} + 4Z_CZ_{Br}\frac{\sin 1.81\,x}{1.81\,x} + 4Z_OZ_{Br}\frac{\sin 2.52\,x}{2.52\,x} + 2Z_{Br}^2\left(1 + \frac{\sin 1.97\,x}{1.97\,x}\right) + Z_C^2 + Z_O^2 \qquad (4)$$

which is based on the same model as phosgene. The carbon–oxygen interatomic distance in carbonyl chloride and bromide (1.13 Å.) agrees well with the values obtained for formaldehyde (1.15 Å.) by electron diffraction,[16] and 1.2 Å. from the absorption spectra.[17] The absorption spectrum of phosgene[18] indicates a plane "Y" structure similar to formaldehyde. An angle greater than 110° might be expected in carbonyl chloride and bromide since an angle of 125° was found in the methylene halides. This difference seems reasonable when the interaction of the dipoles is considered. The repulsion between the carbonyl group and the halogen atoms is probably equal to the mutual repulsion of the halogen atoms.

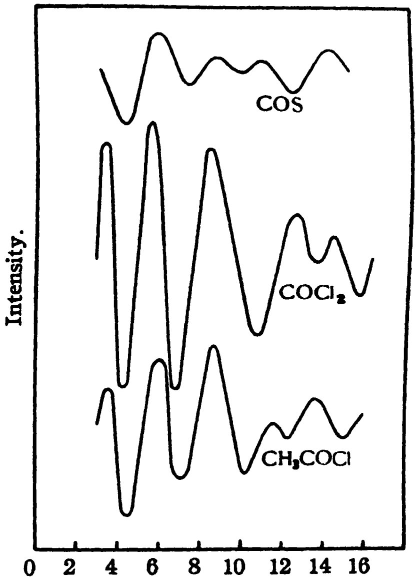

Fig. 2.—Theoretical intensity curves.

The effect of the hydrogen atoms was neglected in the intensity curves for acetyl chloride and bromide. The hydrogen–oxygen and hydrogen–halogen interatomic distances are variable if free rotation occurs around the carbon–carbon bond. Intensity curves were calculated for plane structures with 115, 125 and 135° angles between the carbon–oxygen and carbon–halogen bonds. A slightly better correlation of the maxima was

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(15) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 498 (1932).

(16) L. Bru, *Añales soc. españ. fís. quím.*, **30**, 483 (1932).

(17) V. Henri and S. A. Schou, *Z. Physik*, **49**, 774 (1928).

(18) V. Henri and O. R. Howell, *Proc. Roy. Soc.* (London), **A128**, 178 (1930).

possible for the usual tetrahedral model. The intensity equation for acetyl chloride is

$$\frac{I}{k} = 2Z_CZ_O\left(\frac{\sin x}{x} + \frac{\sin 2.11\,x}{2.11\,x}\right) + 2Z_C^2\left(1 + \frac{\sin 1.36\,x}{1.36\,x}\right) + 2Z_CZ_{Cl}\left(\frac{\sin 1.62\,x}{1.62\,x} + \frac{\sin 2.44\,x}{2.44\,x}\right) + 2Z_OZ_{Cl}\frac{\sin 2.34\,x}{2.34\,x} + Z_O^2 + Z_{Cl}^2 \qquad (5)$$

and the equation for acetyl bromide is

$$\frac{I}{k} = 2Z_CZ_O\left(\frac{\sin x}{x} + \frac{\sin 2.11\,x}{2.11\,x}\right) + 2Z_C^2\left(1 + \frac{\sin 1.36\,x}{1.36\,x}\right) + 2Z_CZ_{Br}\left(\frac{\sin 1.82\,x}{1.82\,x} + \frac{\sin 2.62\,x}{2.62\,x}\right) + 2Z_OZ_{Br}\frac{\sin 2.53\,x}{2.53\,x} + Z_O^2 + Z_{Br}^2 \qquad (6)$$

For these molecules the angle between the carbon–carbon bond and the carbon–halogen bond is 110 ± 10° while the other angles are each 125 ± 10°. The molecular structures of acetyl chloride and bromide are quite similar to the structure of acetone[19] which has been determined by the same method. Interatomic distances common to the three structures are in agreement.

Summary

The molecular structures of carbonyl sulfide, chloride and bromide, acetyl chloride and bromide have been investigated by electron diffraction. The results are in agreement with other structural determinations. Carbonyl sulfide has been found to have a linear structure. The other molecules have been represented by plane "Y" models. An angle of 110° has been found between the halogen atoms of carbonyl chloride and bromide. The tetrahedral model has been found for acetyl chloride and bromide. The carbon–oxygen interatomic distance has been found constant in the carbonyl compounds.

BERKELEY, CALIFORNIA

RECEIVED JULY 24, 1933
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[19] J. Hengstenberg and L. Bru, *Añales soc. españ. fis. quim.*, **30**, 341 (1932).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

An Azeotropic Mixture of Secondary Butyl Alcohol and Secondary Butyl Bromide[1]

BY DAVID F. HOUSTON

An azeotropic (constant boiling) mixture of secondary-butyl alcohol and secondary-butyl bromide recently encountered in our work apparently is not recorded in the literature. The following study of this mixture has been made.

Experimental

Sec-butyl Alcohol.—Commercial *sec*-butyl alcohol[2] was fractionated in a six-plate bubbling-cap still,[3] without a Cottrell boiler, but with a thermometer immersed in the vapors. The fraction boiling at 99.4 to 100.5° was dried over anhydrous sodium sulfate, distilled over freshly ignited lime, and the constant boiling fraction collected. The refractive index and boiling point of the product are shown in Table I.

Sec-butyl Bromide.—A 50% excess of phosphorus tribromide was added dropwise to the commercial alcohol, cooled in ice water. The mixture was heated for one-half hour on the steam-bath, cooled and poured onto cracked ice. The oily layer was separated, distilled, thoroughly washed with water and 10% sodium carbonate solution, and dried over calcium chloride. The bromide was fractionated in the bubbling-cap still. The refractive index and boiling point of the constant boiling fraction are given in Table I.

Azeotropic Mixture.—A mixture of 150 ml. each of the alcohol and the bromide was distilled slowly from the bubbling-cap still. During a fore-run of about 20 ml., the temperature rose to 87.2°, where it remained while 155 ml. of the mixture was obtained. It then rose to the boiling point of the alcohol and again became constant. The refractive index and boiling point of the azeotropic mixture are given in Table I.

Composition of the Azeotropic Mixture.—From a curve drawn by plotting the refractive indices, at 20°, of a series of alcohol–bromide mixtures against the mole per-

TABLE I

BOILING POINTS AND REFRACTIVE INDICES

Material		n^{20}_D	B. p., *corr.*, °C., at 760 mm.
Sec-butyl alcohol	Present material	1.3983	99.5 ± 0.1
	Previously reported	1.3970[a]	99.50[b]
Sec-butyl bromide	Present material	1.4370	91.3 ± 0.1
	Previously reported	1.4372[c]	91.25[d]
Azeotropic mixture		1.4256	87.2 ± 0.1 (749 mm.)

[a] J. Timmermans and F. Martin, *J. chim. phys.*, **25**, 432 (1928). Calculated from value at 15° and the coefficient $\Delta n/\Delta t$ 0.00049 given in this reference. [b] *Ibid.*, p. 431. [c] G. V. Wendell, *Am. Chem. J.*, **26**, 318 (1901). Calculated from value given at 25.25° and the coefficient $\Delta n/\Delta t$ 0.00054 determined on the present material. [d] J. Timmermans, *Bull. soc. chim. Belg.*, **36**, 504 (1927).

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[1] Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Stanco Distributors, Inc., New York City, kindly supplied a quantity of this alcohol. Their assistance is hereby gratefully acknowledged.

[3] J. H. Bruun and S. T. Schicktanz, *Bureau of Standards Journal of Research*, **7**, 851–882 (1931).

centages of the bromide, the azeotropic mixture was found to contain 70.7 mole per cent. of *sec*-butyl bromide. Data for the series of mixtures are shown in Table II.

Bromine was directly determined in the constant boiling fraction by the method of Lemp and Broderson.[4] These determinations gave values of 71.0 and 71.4 mole per cent. of bromide in the mixture.

TABLE II

REFRACTIVE INDICES OF MIXTURES OF SEC-BUTYL ALCOHOL AND BROMIDE

Weight per cent. of bromide	....	15.02	27.39	39.08	51.70	60.06	70.41	79.25	84.85	93.34	100
Mole per cent. of bromide	....	8.51	16.94	25.75	36.67	44.86	56.27	67.36	75.20	88.33	100
n^{20}_{D}	1.3983	1.4013	1.4042	1.4073	1.4117	1.4138	1.4192	1.4242	1.4275	1.4329	1.4370

Conclusion

Secondary-butyl alcohol and secondary-butyl bromide form an azeotropic mixture boiling at 87.2° at 749 mm., having a refractive index n^{20}_{D} of 1.4256, and containing 71.0 ± 0.4 mole per cent. of the bromide.

[4] J. F. Lemp and H. J. Broderson, THIS JOURNAL, 39, 2069–2074 (1917).

WASHINGTON, D. C.

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Note

Copper Selenate Tetrammine Dihydrate

BY WILLY LANGE AND GERDA V. KRUEGER

We recently described a method for preparing copper selenate tetrammine dihydrate in large crystals.[1] Slight variations in the procedure, however, often result in failure and occasionally no crystals at all are deposited from the ammoniacal solution. We have now perfected two new procedures which are entirely dependable.

(1) Fifteen grams of crystalline copper selenate (Kahlbaum) is dissolved by boiling in 25 cc. of 25% aqueous ammonia and, after filtering and cooling with ice, alcohol is added, the precipitate filtered off, washed with acetone and ether, and dried on a porous plate. Ten grams of this product is dissolved, for the greater part, by warming in 8 to 10 cc. of 25% aqueous ammonia and the hot solution is filtered as quickly as possible but without suction. The hot filtrate is then placed in a closed Erlenmeyer flask partially submerged in a large amount of hot water so that it will cool slowly. It is important that the solution be not shaken during this period.

(2) The same procedure is followed except that the hot solution in the Erlenmeyer flask is rapidly chilled to room temperature, whereupon needles of monohydrate precipitate. These are redissolved, for the greater

[1] THIS JOURNAL, 53, 4013 (1931).

part, by adding carefully drops of the aqueous ammonia, the remainder of the crystals being dissolved by cautiously warming the closed flask. On cooling to room temperature no immediate precipitation occurs, but on being kept undisturbed in an ice refrigerator which maintained in general a temperature between 8 and 12°, but sometimes was even colder, crystals begin to deposit after two or three days.

Both of these methods always yield hexagonal crystals of the tetrammine dihydrate.

When a fresh quantity of crude dihydrate was dissolved, by warming, in the final filtrate obtained by the first method, on cooling, long needles of the monohydrate appeared. When the closed Erlenmeyer flask containing these crystals was allowed to stand at room temperature for three months, with a daily variation of 4 or 5°, the needles of the monohydrate were slowly absorbed and replaced by the large six-sided plates of dihydrate until finally only the dihydrate, analytically pure, in typical hexagonal tablets remained. The final solution contained 19.3% of ammonia which was, of course, partly in the copper complex.

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[CONTRIBUTION FROM THE UNIVERSITY OF SYDNEY]

Some Arsine Derivatives of Silver Salts

BY G. J. BURROWS AND R. H. PARKER

Various compounds of silver salts with basic substances are described in the literature. In most of these silver has a coördination valency of two. Thus silver halides (or nitrate) are known to combine with two molecules of ammonia, pyridine, aniline, quinoline, etc.[1] In addition, silver ammines have been described with compositions corresponding to the formulas, $AgCl\cdot NH_3$, $AgCl\cdot 3NH_3$ and $2AgCl\cdot 3NH_3$.

It was decided to investigate the action of phenyldimethylarsine and diphenylmethylarsine on silver salts. These two particular arsines were chosen on account of their ease of preparation and the fact that they are known to combine with the iodides of phosphorus, arsenic, antimony, bismuth and tin.[2] When silver chloride was digested with an aqueous alcoholic solution of phenyldimethylarsine a clear solution was readily obtained, from which white needles separated on cooling. These, on examination, were found to be bisphenyldimethylarsine silver chloride $[Ag(PhMe_2As)_2]Cl$. Compounds of other silver salts with phenyldimethylarsine and diphenylmethylarsine were prepared and examined. The

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(1) *Cf.* Weinland, "Einfuhrung in die Chemie der Komplex-Verbindungen," p. 270.

(2) Burrows and Turner, *J. Chem. Soc.* 119, 1449 (1921).

compounds isolated were all of the same type, the coördination valency of the silver being two. The relative proportions of silver salt and arsine were varied in attempts to obtain the analogs of the other ammine silver salts described, but in all cases the compound isolated was one in which two molecules of arsine were coördinated with one atom of silver.

The arsine derivatives are white crystalline compounds with characteristic melting points and are quite stable and unaffected by light. The following list, containing the salts so far prepared, illustrates the variations in melting point.

Bis-phenyl Dimethyl and Bis-diphenyl Methyl Arsine Silver Salts

		Yield, %	M. p., °C.	Arsenic, %			Silver halide, %	
				Calcd.	Found		Calcd.	Found
Diphenyl methyl	Chloride	60	121	23.8	23.5		22.7	22.4
	Bromide	50	110	22.2	21.9		27.8	27.6
	Iodide	..	132	..	..		32.5	32.5
	Nitrate	81	112	..	..	Ag,	16.2	16.3
Phenyl dimethyl	Chloride	..	97	29.6	29.2		28.3	28.1
	Bromide	..	79	..	..		34.1	33.9

It is interesting to note that the bromide has a lower melting point than the corresponding chloride in both series, while in the case of diphenylmethylarsine derivatives the iodide has the highest melting point. The iodide can only be prepared from the nitrate and as we have been unable to prepare the nitrate in the case of phenyldimethylarsine the corresponding iodide could not be isolated. Attempts to prepare arsine silver sulfate were also unsuccessful.

Although the chlorides and bromides are easily prepared by heating the silver halide and arsine in aqueous alcohol and allowing to cool, it was found that they could not be redissolved in aqueous alcohol or absolute alcohol or methyl alcohol except in the presence of excess of the arsine; the compounds appear to be decomposed on heating in these solvents. The halides are also insoluble in acetone, ether and benzene, undergoing decomposition on heating in the two latter liquids with loss of arsine. Bisdiphenylmethylarsine silver nitrate is remarkable in being soluble in aqueous alcohol, ethyl or methyl alcohol, acetone or benzene.

Unsuccessful attempts were made to isolate arsine derivatives of silver salts of optically active acids such as *d*-mandelic and *d*-bromocamphor sulfonic acids. Experiments were carried out with both diphenylmethylarsine and phenylmethylethylarsine. A derivative of the latter should contain arsenic as a center of asymmetry and it was therefore hoped that fractions differing in optical activity would be obtained. On warming the arsine and silver salt in alcohol, reaction undoubtedly took place and a clear solution was obtained but this could not be induced to crystallize. On concentrating the solution *in vacuo* a thick sirup (and ultimately a glassy residue) resulted which very slowly darkened on keeping. This portion of the investigation is being studied further.

Experimental

For the preparation of bis-diphenylmethylarsine silver chloride or the corresponding bromide, freshly precipitated silver chloride (1 mol) or silver bromide was well washed with hot water, then with 96% alcohol. It was then treated in hot alcohol on the water-bath with diphenylmethylarsine (2 mols) until the silver halide had dissolved. On cooling the complex salt separated in white needles. These were removed and washed once with ether. (N. B. Excessive treatment with ether appears to decompose the compound by removal of arsine.) A further crop of crystals was obtained by careful concentration of the mother liquor.

These compounds do not darken on exposure to light; they are insoluble in water, alcohol, acetone, ether or benzene. They are decomposed by concentrated nitric acid. In the analysis, a known weight was treated with excess of silver nitrate (crystals) and a few cc. of concentrated nitric acid and the silver halide precipitate well washed with water, and then alcohol (or acetone) and dried.

Bis-diphenylmethylarsine Silver Nitrate $[Ag(Ph_2MeAs)_2]NO_3$.—This compound was very readily obtained by adding an aqueous alcoholic solution of diphenylmethylarsine (2 mols) to a saturated solution (aqueous) of silver nitrate (1 mol). On agitating the solution the complex salt separated as a micro crystalline precipitate. This was washed with a little ether and dried over sulfuric acid.

Bis-diphenylmethylarsine Silver Iodide $[Ag(Ph_2MeAs)_2]I$.—Attempts to prepare this compound by the action of the arsine on silver iodide were unsuccessful. The relative solubilities of silver chloride, bromide and iodide in diphenylmethylarsine are similar to their relative solubilities in ammonia. The iodide was prepared from the nitrate. An aqueous alcoholic solution of bisdiphenylmethylarsine silver nitrate was treated with the calculated quantity of hydriodic acid, when a very pale yellow finely crystalline precipitate separated. This was filtered off, washed with a little ether and dried over sulfuric acid. It is quite insoluble in the ordinary solvents. During an analysis of this compound it was noticed that on warming with nitric acid and excess of silver nitrate the substance melted and crystallized on cooling. The crystalline mass was removed, washed with water, alcohol and finally ether. It melted at 113° and on analysis was found to be the nitrate.

When decomposed with nitric acid alone, silver iodide is formed, and this can be filtered and washed with acetone or alcohol and weighed.

Bis-phenyldimethylarsine silver chloride and the corresponding bromide were prepared in a similar manner to the bis-diphenylmethylarsine silver compounds using phenyldimethylarsine in place of diphenylmethylarsine. Their solubilities resemble those of the other series.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates.[1] IV. Cumulative Extraction[2] of Kero Bases.[3] The Isolation of 2,4,8-Trimethylquinoline among the Kero Bases

BY T. S. PERRIN AND J. R. BAILEY

Introduction.—The kero bases represent a very complex mixture of both aromatic and non-aromatic types in a percentage ratio of approximately 15:85, respectively. Especially as concerns the non-aromatic bases, the direct isolation of pure products from distillation fractions can be attained through fractional crystallization of their salts only in exceptional cases.

It is obvious that a practical method of separation of the bases into aromatics and non-aromatics, would simplify the isolation of individual products. Based on the observation of a wide difference in the distribution ratio of salts of the two families between water and certain solvents immiscible with water, a process, which accomplishes this end in a most satisfactory way, has been perfected and found of general application over the entire range of kero bases.

The present investigation has disclosed a ready solubility of the hydrochlorides of the non-aromatic bases in chloroform, as compared with a lesser solubility of the aromatic hydrochlorides, and among the latter are included the hydrochlorides of both pyridine and quinoline homologs. Furthermore, the non-aromatic hydrochlorides are very soluble in water, whereas corresponding salts of some of the methylated quinolines encountered crystallize nicely from water.

In resolution of petroleum bases into the two types, the following procedure will be found serviceable, where either crude bases or distillation fractions are employed. The bases are dissolved in an excess of 1:1 hydrochloric acid and the solution extracted with an equal volume of chloroform. Instead of chloroform, ethylene chloride may be used and, on account of the much lower cost, it should prove serviceable in industrial extraction. The initial chloroform extraction effects a high concentration of the aromatic hydrochlorides in the aqueous layer and of the non-aro-

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(1) The investigation of organic nitrogen bases from the crude kerosene distillate of California petroleum was originally undertaken in connection with American Petroleum Institute Project 20, entitled: "Isolation and Investigation of Nitrogen Compounds Present in Petroleum."

For this research the Union Oil Company of California furnished the material, consisting of bases which were assembled when the refinery was operating largely on McKittrick crude from the San Joaquin Valley field and having a nitrogen content of 0.64%. Only recently the Texas Laboratory received three barrels of bases obtained from 3000 barrels of Edeleanu kerosene extract. This sulfur dioxide extract represents 25% of the kerosene fraction and the latter 5% of the crude oil refined; so it is evident that 80,000 barrels of California petroleum yield approximately 1 barrel of kero bases. However, all the crude distillates contain bases; so their aggregate amount would be considerably larger, were the gasoline, gas oil and lubricating oil fractions included.

(2) "Cumulative extraction" is explained in the text.

(3) "Kero bases" is an abbreviation for "kerosene bases."

matic hydrochlorides in the chloroform layer. In further segregation, the water layer is extracted several times with chloroform and the chloroform layer several times with water. Since there is always an appreciable difference in the refraction of the two types of bases within any boiling point range, refractive index determinations offer a convenient control at every stage of the process.

Its extensive application seems to warrant a specific name for this process and "Cumulative Extraction" is proposed, as embodying in a concise way the general result attained in progressive concentration of the aromatic hydrochlorides in water and the non-aromatic hydrochlorides in chloroform.

Cumulative extraction has been of especial service in simplifying isolations already accomplished by other methods, and in extending this work. Previous papers of this series have reported the isolation of 2,3,8-trimethylquinoline,[4] b. p. 280°, and of a naphthenic base of the formula $C_{16}H_{25}N$, b. p. 278.2°.[5] By the distribution of the salts of the fraction containing these two bases between water and chloroform, the separation and purification has been simplified greatly, and a third substance, 2,4,8-trimethylquinoline, has been isolated from the same distillation fraction (275° zone). The new procedure has been of further use in separation of 2,3- and 2,4-dimethylquinoline from the fractions in the 265° zone, and it is superior to an alternate method, described in Paper V of this series and which makes use of sulfur dioxide. Paper VI records the isolation, by cumulative extraction, of 2,8-dimethylquinoline from the 253° fraction of bases.

In final separation of the aromatics from small amounts of non-aromatics, either the free bases or their hydrochlorides can be converted in acetone solution to sulfates. The aromatic sulfates in great part separate from the solvent in crystalline form and the non-aromatic sulfates remain dissolved. It is evident also that both types of hydrochlorides can be converted directly to picrates, as well as mercuric chloride and zinc chloride double salts; however, corresponding salts of non-aromatic bases separate from mixtures almost invariably as non-crystallizing smears. It will be found advisable in picrating hydrochlorides to buffer the solution with sodium acetate; otherwise, where an excess of picric acid is used, it precipitates along with the picrates.

The employment of cumulative extraction has revealed the presence of aromatics and non-aromatics in all distillation fractions of kero bases. The boiling points and refractivities of several products, encountered below the quinoline range, indicate pyridine homologs. Where an aromatic base of known boiling point is suspected, it will be found, if present, in maximum concentration in a fraction boiling 3 to 5° lower than its own boiling point and, even when present in very small amount, it can be segregated from accompanying non-aromatics until its isolation in pure form is greatly simplified. A search for the common coal-tar bases, quinoline, isoquinoline, quinaldine and lepidine has given only negative results.

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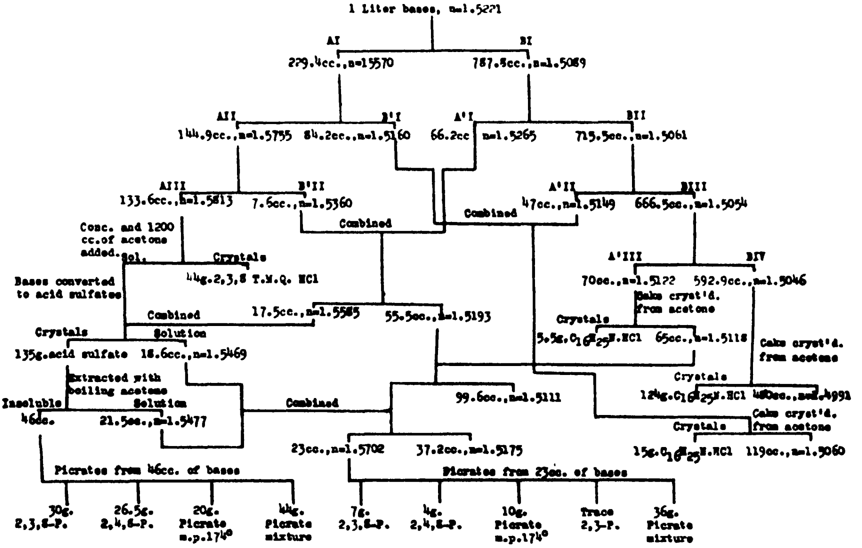
[4] W. A. King and J. R. Bailey, THIS JOURNAL, 52, 1245 (1930).

[5] W. C. Thompson and J. R. Bailey, *ibid.*, 53, 1002 (1931).

Experimental Part

Cumulative Extraction of a Distillation Fraction of Kero Bases Boiling at 273° and with n_D^{27} 1.5221.—One liter of bases[6] in one liter of 1:1 hydrochloric acid was extracted with 1200 cc. of chloroform and the aqueous layer AI separated from the chloroform layer BI. AI was washed with 400 cc. of chloroform, yielding fractions AII and B'I, followed by extraction of AII with 250 cc. of chloroform to yield fractions AIII and B'II. In a similar way BI was extracted with three successive portions of water, 400, 400 and 1000 cc., being split finally into fractions A'I, A'II, A'III and BIV. The accompanying flow-sheet is self-explanatory.



Flow-sheet in cumulative extraction.

"A" refers to hydrochlorides in water. "B" refers to hydrochlorides in $CHCl_3$. "n" = "n_D^{27}." "Cake" refers to residue after removal of solvent. "2,3,8-P" and "2,4,8-P" = "Picrates of 2,3,8- and 2,4,8-trimethylquinoline," respectively. "2,3-P" = "2,3-Dimethylquinoline picrate." Volumes, where given, refer to free bases.

The volumes of bases were arrived at by measuring the oil liberated with caustic soda from a fractional part of the hydrochloride solutions. The samples, after being dried, were used for refractivity determinations and finally converted to hydrochlorides before recombination with the fractions from which they were taken. A list of the end-products from processing the one liter of bases follows: 44 g. of 2,3,8-trimethylquinoline hydrochloride; 37 g. of 2,3,8-trimethylquinoline picrate; 30.5 g. of 2,4,8-trimethylquinoline picrate; 30 g. of unknown picrate, m. p. 174°; 80 g. of mixture of low melting picrates; 144.5 g. of hydrochloride of the $C_{16}H_{25}N$ base; 735.8 g. of non-aromatic bases (4 fractions, n_D^{27} 1.4991 to 1.5175).

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(6) This material was purposely not exhaustively fractionated.

Isolation of 2,4,8-Trimethylquinoline.—This product was encountered by King and Bailey[7] at the time 2,3,8-trimethylquinoline was discovered, but was not identified.

After concentration of the aromatic bases by cumulative extraction of the 273° fraction, the ready solubility of 2,4,8-trimethylquinoline hydrochloride in water and of its

TABLE I

EVALUATION OF THE AROMATIC AND NON-AROMATIC CONTENT OF DISTILLATION FRACTIONS OF KERO BASES

No. of distil.	B. p. and refr. of original samples B. p., °C.	n^{27}_D	Admixed hydrocarbon oil Vol., cc.	n^{27}_D	Vol. and refr. of bases in water layer Vol., cc.	n^{27}_D	Vol. and refr. of bases in $CHCl_3$ layer Vol., cc.	n^{27}_D	Bases in water layer, %
IV	182	1.4816	2.1	1.4600	3.2	1.4918	4.7	1.4860	40.6
III	193	1.4898	0.8	1.4910	3.9	1.4930	5.3	1.4851	42.4
IV	196	1.4888	.5	1.4687	4.1	1.4912	5.4	1.4832	43.2
V	200	1.4888	.4	1.4851	3.9	1.4951	5.7	1.4857	40.6
IV	205	1.5006	Naphthalene cryst.						
				1.5878	2.1	1.4916	5.1	1.4830	29.2
IV	210	1.5009	0.5	1.5031	3.3	1.5046	6.2	1.4882	34.8
IV	215	1.5029	.3	1.5169	3.1	1.5068	6.6	1.4940	32.0
IV	220	1.5008	.2	1.5110	3.3	1.5044	6.5	1.4940	33.7
IV	225	1.5092	Trace		1.1	1.5252	8.9	1.4985	31.0
IV	230	1.5108	Trace		1.4	1.5348	8.6	1.5009	14.0
III	235	1.5050	None		1.5	1.5152	8.5	1.4997	15.0
IV	240	1.5090	0.2	1.5311	1.5	1.5342	8.3	1.5011	15.3
IV	245	1.5000	Trace		0.8	1.5190	9.2	1.4951	8.0
IV	250	1.5103	Trace		1.5	1.5326	8.5	1.5040	15.0
V	255	1.5137	Trace		1.3	1.5448	8.7	1.4960	13.0
IV	260	1.5138	Trace		1.0	1.5519	9.0	1.5064	10.0
V	265	1.5145	Trace		1.1	1.5565	8.9	1.5050	11.0
IV	270	1.5201			1.4	1.5690	8.6	1.5077	14.0
V	275	1.5262			1.9	1.5760	8.1	1.5107	19.0
IV	280	1.5330			2.3	1.5739	7.7	1.5151	23.0
V	285	1.5418			2.7	1.5733	7.3	1.5230	27.0
IV	288	1.5428			3.1	1.5709	6.9	1.5323	31.0
III	295	1.5468			3.0	1.5732	7.0	1.5311	30.0
III	300	1.5532			3.0	1.5755	7.0	1.5372	30.0
III	305	1.5545			3.1	1.5747	6.9	1.5382	31.0
II	310	1.5623			2.8	1.5755	7.2	1.5486	28.0
II	315	1.5640			2.6	1.5759	7.4	1.5496	26.0
II	320	1.5661			1.9	1.5745	8.1	1.5565	19.0
II	325	1.5662			1.7	1.5762	8.3	1.5561	17.0
II	330	1.5671			1.4	1.5758	8.6	1.5574	14.0
II	335	1.5718			1.0	1.5921	9.0	1.5598	10.0
II	345	1.5910			2.5	1.6200	7.5	1.5720	25.0
II	350	1.5768			1.5	1.6045	8.5	1.5650	15.0

Ten cc. samples from each of the above fractions, dissolved in 10 cc. of 1:1 hydrochloric acid, were carried through a single extraction with 20 cc. of chloroform and then the bases in the aqueous and chloroform layers were precipitated from the dissolved hydrochlorides with an excess of caustic soda. In some cases a small amount of hydrocarbon oil was encountered.

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(7) Ref. 4, p. 1243.

sulfate in acetone facilitated the separation from accompanying 2,3,8-trimethylquinoline. Final purification was effected through the picrate, which crystallizes from alcohol in slender rectangular plates melting at 193°.

The boiling point of 269–270° (pressure not given) for 2,4,8-trimethylquinoline, as recorded in the literature,[8] does not agree with our determination of 280° (corr.) at 746 mm. on both the synthetic product and the kero base. For this quinoline n^{50}_{D} is 1.5855.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.21; H, 7.60; N, 8.19. Found: C, 84.43; H, 7.42; N, 8.35.

Phthalone of 2,4,8-Trimethylquinoline.—The base and the calculated amount of phthalic anhydride are heated for three hours at 200°, the melt is dissolved in concentrated sulfuric acid and the solution is poured onto crushed ice. The phthalone crystallizes from alcohol in yellow microscopic needles melting at 282°.

Anal. Calcd. for $C_{20}H_{15}O_2N$: C, 79.73; H, 4.98; N, 4.65. Found: C, 79.65; H, 5.16; N, 4.71.

Comparative Efficiency of the Cumulative Extraction and Sulfur Dioxide Processes in Segregation of Aromatic Bases.—600 cc. of residual bases of the 263–267° fraction from which 2,3- and 2,4-dimethylquinoline had been isolated by the use of sulfur dioxide, as described in Paper V of this series, was carried through cumulative extraction. It developed that, whereas sulfur dioxide had removed 2,4-dimethylquinoline completely, an additional 5 g. of the 2,3-isomer could be recovered. The difficult solubility of the picrate of this base in alcohol simplified its purification. There was also encountered here in small amount a new $C_{12}H_{13}N$ base for which proof of structure and synthesis is under way.

Cumulative Extraction in Evaluation of the Nature and Amount of Aromatic Bases in Distillation Fraction.—The subjoined table gives the results from cumulative extraction of kero bases, within the b. p. range of 182–350°. The samples above 300° were imperfectly fractionated. It is probable that both aromatic and non-aromatic hydrochlorides of these bases exhibit within the two types a considerable variance in relative solubilities in water and chloroform, so frequently the initial chloroform extraction does not furnish a true picture of the proportionate amounts of the two types. However, from cumulative extraction when applied exhaustively—and this is possible with 10-cc. samples—estimates reliable within narrow limits of error can be reached.

The aromatic bases in the 182–220° fractions consist mainly of pyridine homologs, where an average n^{25}_{D} value[9] around 1.5000 may be expected. In fractions above 220° pyridines will probably not be encountered. Since quinoline homologs have an n^{20}_{D} value around 1.6000, the deduction follows from the data in Table I that fractions above 330° contain an appreciable quantity of aromatic bases of a higher order than quinolines.

Summary

Based on a wide difference in the distribution ratio of the hydrochlorides of aromatic and non-aromatic petroleum bases between water and chloroform, a method of segregation of the two types, for which the name "Cumulative Extraction" is proposed, has been developed. This process is now a standardized and reliable procedure of general application. The isolation by this method of 2,4,8-trimethylquinoline and a second $C_{12}H_{18}N$ base of unknown structure is described.

Austin, Texas

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[8] S. Yamaguchi, *J. Pharm. Soc., Japan*, pp. 5–6 (1924); *Chem. Zentr.*, 98, 1837 (1927).

[9] *Cf.* Takashi Eguchi, *Bull. Chem. Soc. Japan*, 3, 241 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. V. The Use of Sulfur Dioxide in the Separation of Petroleum Bases

BY BURNARD S. BIGGS AND JAMES R. BAILEY

Introduction.—Although the behavior of organic bases toward sulfur dioxide has been studied quite extensively,[1] apparently this reaction has not been employed as an agency in separation of mixtures of amines.

Sulfur dioxide forms addition compounds with both aromatic and non-aromatic bases, but it remains to be determined whether all kero bases enter into such combinations. Some of these products are stable at temperatures as high as 100°, while others have been found to dissociate quite rapidly at room temperature. Advantage has been taken of the differences in the relative stability and solubilities of these sulfur dioxide addition compounds to effect a partial separation of the kero bases.

The sulfur dioxide process is unsatisfactory, in that it does not effect quantitative separations. Also addition products of some of the non-aromatic bases layer out, and subsequent separation of individual aromatic bases in the form of picrates is retarded through the formation of smears.

Experimental Part

A 2000-cc. fraction of bases of b. p. 263–267° was dissolved in an equal volume of anhydrous ether, and sulfur dioxide was led in at room temperature to saturation. At first a small amount of oil separated which later redissolved. The excess of sulfur dioxide, along with part of the solvent, was allowed to evaporate to the point where a heavy viscous oil layered out, and then sufficient ether was added to restore the original volume. The supernatant layer was decanted and the viscous residue was washed with ether, dissolved in a little alcohol and treated with a slight excess of an alcoholic solution of picric acid. After complete precipitation, the picrates were washed with sufficient alcohol to remove smeary admixtures.

The alcoholic filtrate contained a considerable amount of non-aromatic picrates of a greater solubility in organic solvents than the aromatic salts. It may be that here the relative concentration of the various non-aromatics was decidedly different from that in the original fraction of bases, and in that event there is suggested an application of the sulfur dioxide reaction in partial resolution of non-aromatic mixtures.

Isolation of 2,4-Dimethylquinoline.—When the crystalline picrates were treated with an amount of hot glacial acetic acid sufficient to leach out the more soluble portion, 2,4-dimethylquinoline picrate separated from the filtered solution in long orange colored needles and was recrystallized several times from 95% alcohol, with filtration carried out around 40° to avoid the separation of admixtures. Finally a product melting at 194° was obtained.

2,4-Dimethylquinoline, synthesized according to Otto Fischer,[2] proved identical with the base obtained from the picrate of m. p. 194°. Furthermore, the kero base

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(1) Schiff, *Ann.*, 140, 125 (1866); 144, 49 (1867); Michaelis, *Ber.*, 24, 749 (1891); Glebocka and Korczynski, *Gazz. chim. ital.*, 50, 378 (1920); Woroshtzow, *Ber.*, 63, 2354 (1930); Hill, THIS JOURNAL, 53, 2598 (1931).

(2) Otto Fischer, *Ber.*, 19, 1037 (1886).

and the synthetic product were shown to be identical through comparison of several salts. Both the synthetic and the kero base boiled at 274° at 756 mm.[3]

Isolation of 2,3-Dimethylquinoline.—The picrates, referred to above as difficultly soluble in glacial acetic acid, were recrystallized from this solvent in the form of microscopic hexagonal prisms melting at 231°. The base, liberated from the purified picrate, proved identical with 2,3-dimethylquinoline, synthesized by the method of Eliasberg and Friedländer.[4] Several salts made from both the kero and the synthetic base were compared. The base itself is a white crystalline solid melting at 67° and boiling at 273° (750 mm.).[5]

All the filtrates obtained in the separation of the 2,3- and 2,4-dimethylquinoline picrates were combined and concentrated to a small volume, when a third picrate melting at 160° separated in radiating clusters of needles. This product is referred to in Paper IV by Perrin and Bailey, who find that, when pure, it melts at 174°.

ANALYTICAL DATA ON THE TWO KERO BASES AND THEIR SALTS

	Calcd.			Found		
	C	H	N	C	H	N
2,3-Dimethylquinoline	84.08	7.01	8.92	84.08	7.15	8.98
2,4-Dimethylquinoline	84.08	7.01	8.92	83.83	7.10	9.05
2,3-Dimethylquinoline picrate	52.85	3.63	14.51	52.80	3.66	14.52
2,4-Dimethylquinoline picrate	52.85	3.63	14.51	52.89	3.64	14.74
2,4-Dimethylquinoline chloroplatinate	...	..	3.86	...	..	3.84
2,3-Dimethylquinoline acid sulfate	...	..	5.49	...	..	5.25

Summary

The additive reaction of sulfur dioxide on amines has been applied to the isolation of 2,3- and 2,4-dimethylquinoline from a distillation fraction of kero bases in the 263–267° range.

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(3) C. Beyer, *J. prakt. Chem.*, **33**, 401 (1885), reports a b. p. of 264–265° (uncorr.) with no mention of pressure.

(4) J. Eliasberg and P. Friedländer, *Ber.*, **25**, 1754 (1892).

(5) G. Rohde, *ibid.*, **22**, 269 (1889), reports an uncorrected b. p. of 261° at 729 mm.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. VI. The Occurrence of 2,8-Dimethylquinoline in the Crude Kerosene Distillate of California Petroleum

BY G. R. LAKE AND J. R. BAILEY

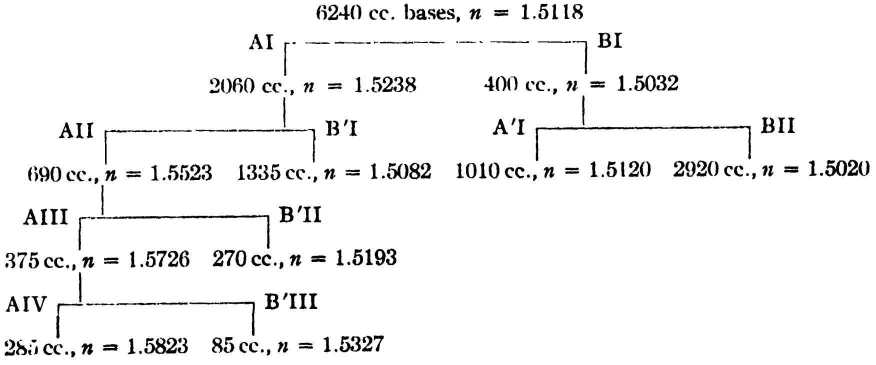
Introduction.—All the quinolines so far encountered among the kero bases are 2, 3, 4 or 8 polymethyl homologs *with one methyl at position 2;* no quinoline substituted at positions 5, 6 or 7 has been identified. Whereas quinaldine is the only coal-tar quinoline yielding a phthalone (Quinoline Yellow), petroleum offers in synthesis of this class of dyes[1] a wealth of intermediates none of which has been obtained from any other natural source.

When the present investigation was begun, two of the three possible dimethylquinolines, with one methyl in position 2 and the other at position 3, 4 or 8, were known to exist among the kero bases,[2] but the 2,8-isomer[3] had not been encountered. Employing cumulative extraction on the 253–256° fractions, we have found 2,8-dimethylquinoline and established its identity with the synthetic base.

Experimental Part

Cumulative Extraction of the 253–256° Fraction of Kero Bases.—A quantity of this fraction was distributed between equal volumes of 1:1 hydrochloric acid and chloroform, and the two solutions were extracted further according to the method described in Paper IV.[4] The results are summarized in the subjoined flow sheet (see paper IV for an explanation of the symbols).

FLOW SHEET



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(1) *Cf.* A. Eibner, *Ber.*, **37**, 3605 (1904).

(2) See Paper V of this series by Biggs and Bailey.

(3) (a) O. Doebner and W. von Miller, *Ber.*, **16**, 2469 (1883); **23**, 2259 (1890); (b) A. Eibner and Frz. Peltzer, *ibid.*, **33**, 3467 (1900); **34**, 2450 (1901); (c) M. Wyler, *ibid.*, **60**, 398 (1927); (d) Max Möller, *Ann.*, **242**, 309 (1887).

(4) Perrin and Bailey, THIS JOURNAL, **55**, 4136 (1933).

Final data from processing 6240 cc. of bases into six fractions are

	1	2	3	4	5	6
n^{25}_{D}	1.5832	1.5327	1.5193	1.5120	1.5082	1.5020
Vol., cc.	285	85	270	1010	1335	2920
Vol., %	4.6	1.4	4.3	17.6	21.4	46.8

Isolation of 2,8-Dimethylquinoline.—The aqueous solution of hydrochlorides marked AIV, representing 285 cc. of bases, *i. e.*, 4.6% of the starting material, was evaporated to a small volume from which on chilling the greater part of the 2,8-dimethylquinoline hydrochloride separated. Smeary admixtures were removed with a small amount of cold acetone, followed by recrystallization of the residue from alcohol. The yield of practically pure hydrochloride was 32 g. (0.4%). In a second extraction of 2250 cc. of bases, carried out more carefully, the yield was increased to 1.8%.

In final purification the hydrochloride was treated with the calculated amount of sodium bisulfate in concentrated aqueous solution and the separated acid sulfate recrystallized from 95% alcohol. Next the picrate, prepared from the acid sulfate in alcoholic solution, was recrystallized from 50% acetic acid and then from water. Finally the base, liberated from the picrate with ammonium hydroxide, was converted to the zinc chloride salt and the latter recrystallized from dilute hydrochloric acid. The base, regained from the zinc chloride salt by dry distillation,[30] gave the following constants: m. p. 24°;[5] b. p. 252.4° (754 mm.); n^{25}_{D} 1.5997; mol. wt. (by Rast micro camphor method) calcd. 157, found 159.

For characterization of the base the phthalone, as well as the following new salts, was prepared.

Acid Sulfate.—The calculated amount of sodium acid sulfate is added to a concentrated solution of the hydrochloride in water and the filtered sulfate crystallized from absolute alcohol in radiating clusters of needles melting at 187°.

Perchlorate, $C_{11}H_{11}N \cdot HClO_4$.—This salt, prepared by adding an aqueous solution of sodium perchlorate to the hydrochloride in water, crystallizes from water in slender rods and from alcohol in fine needle clusters melting at 189°. It is insoluble in the other common solvents with the exception of glacial acetic acid. Owing to its explosive nature concordant results were not obtained in the analysis.

Mercuric Chloride Salt.—Prepared in the usual way in dilute hydrochloric acid, this salt crystallizes from glacial acetic or hydrochloric acid in hair-like needles melting at 211°. Its solubilities are similar to those of the perchlorate.

Phthalone.—The base is heated with the calculated amount of phthalic anhydride for two hours at 200° and the melt crystallized from chloroform, glacial acetic acid or nitrobenzene in long slender rods melting with decomposition at 283°. It is only sparingly soluble in the other common solvents.

ANALYSES ON THE BASE AND DERIVATIVES

	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Base, $C_{11}H_{11}N$	84.08	83.78	7.01	7.13	8.92	9.06		
Phthalone, $C_{19}H_{13}O_2N$	79.41	79.20	4.56	4.73	4.88	5.16		
$C_{11}H_{11}N \cdot H_2SO_4$					5.49	5.72		
$(C_{11}H_{11}N \cdot HCl)HgCl_2$					3.01	3.16	22.87	23.05

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(5) Wyler reports a melting point of 27°.

Summary

This paper reports the isolation of 2,8-dimethylquinoline from the kerosene distillate of California petroleum.

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The Nitrogen Compounds in Petroleum Distillates. VII. New Reactions of the Naphthenic Base, $C_{16}H_{25}N$.[1] A New Naphthenic Base, $C_{13}H_{21}N$

BY B. F. ARMENDT AND J. R. BAILEY

Introduction.—Unrefined California petroleum distillates yield, along with aromatic bases, in preponderant amount a host of non-aromatic bases.[2] Since these non-aromatics represent, not only new substances, but also new structural types, their investigation may be considered of unusual scientific interest. In this connection, it may be mentioned, work is in progress to obtain experimental evidence of a possible structural relationship between the non-aromatic bases and petroleum hydrocarbons.

Because both the isolation and proof of structure of the low-boiling non-aromatic bases might be expected to present the least experimental difficulty, an investigation of fractions within the boiling point range of 215–216° was undertaken. Three barrels of kero bases originally available gave only 708 cc. of this material and from this 20 g. (0.004% of the three barrels) of a base of the formula $C_{13}H_{21}N$ was obtained. Research on this product has been limited to a comparison of its general behavior with that of the $C_{16}H_{25}N$ base.

All attempts to hydrogenate both the $C_{13}H_{21}N$ and the $C_{16}H_{25}N$ base ended in failure. They also resist dehydrogenation, a stability hardly to be expected of true *hydroaromatic* bases, and prolonged heating with alkaline permanganate has no oxidizing effect. The $C_{16}H_{25}N$ compound reacts readily with methyl iodide, but the methiodide of the $C_{13}H_{21}N$ compound is not formed under similar conditions. Attempts to employ the Hofmann reaction in degradation of the $C_{16}H_{25}N$ base were unsuccessful, probably due to rearrangement of the quaternary base to a pseudo form.

From the many theoretical possibilities, there has been selected provisionally formula I, for the $C_{13}H_{21}N$ base and the original structural interpretation of the $C_{16}H_{25}N$ base has been changed to II.

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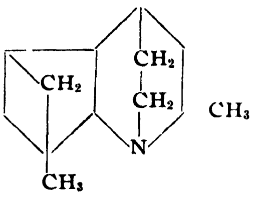
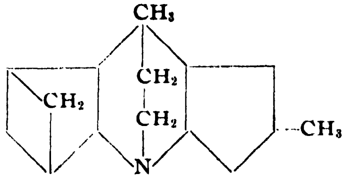
(1) W. C. Thompson and J. R. Bailey, THIS JOURNAL, 53, 1002 (1931).

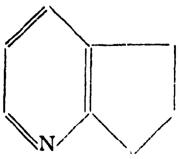
(2) Shale and bones on distillation yield exclusively aromatic bases and the same applies to coal with one exception [Decker and Dunant report the isolation of dihydroacridine from a coal tar distillate, *Ber.*, 42, 1178 (1909)].



I



II



III

The $n^{20}_{\rm D}$ value, 1.4850, of I, as compared with the $n^{20}_{\rm D}$ value, 1.5129, of II, is accounted for by one more ring nucleus in a pyridindacine than in a pyrindine. Furthermore, the refractive difference here of 0.0279 is of the same order as that of 0.0342 between pyridine, where $n^{20}_{\rm D}$ is 1.5068, and 5,7-dihydropyrindine,[3] III, where $n^{20}_{\rm D}$ is 1.5410.

An unexpected observation was that the $C_{16}H_{25}N$ base, just like a quinoline methylated at 2, condenses readily with phthalic anhydride to produce a phthalone.[4] On the other hand, attempts to prepare a phthalone of the $C_{13}H_{21}N$ base gave a negative result. The phthalone of the pyrindacine is of a light orange color and sublimes undecomposed. The presence of a $CH(CO)_2$ complex was established through the preparation of a deep orange colored sodium salt which necessarily involved in its formation enolization of CHCO to C═COH.

Mabery and Wesson[5] in an investigation of "Nitrogen Bases of California Petroleum" found "phthalic anhydride condenses with the basic fractions in what is evidently a phthalone formation," and used this reaction in support of their claim that petroleum bases "consist mainly of alkylated quinolines (or isoquinolines)." It is now evident that phthalone formation cannot be accepted as an infallible test for quinoline bases.

Experimental Part. I

Isolation of the $C_{13}H_{21}N$ Base.—This product was first obtained in a preliminary experiment in an amount sufficient to determine its b. p. 225.6° and the $n^{25}_{\rm D}$ value, 1.4833. Also of importance was the m. p. of the picrate, 158.7°, along with its crystalline form and solubilities. The subjoined data pertain to the material assembled in quest of the $C_{13}H_{21}N$ base and represent combinations of distillation fractions in the order of boiling points:

No.	Cc.	B. p., °C.	$n^{20}_{\rm D}$
I	163	215.3–218	1.4935–1.4972
II	190	220 –221.5	1.4875–1.4905
III	203	223 –224.5	1.4862–1.4880
IV	152	225 –226	1.4858–1.4865

Each of the four batches of bases was extracted with three successive portions of *N*

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(3) Takashi Eguchi, *Bull. Chem. Soc. Japan*, **3**, 239 (1928); *Chem. Zentr.*, **100**, 331 (1928); W. C. Thompson, THIS JOURNAL, **53**, 3160 (1931).

(4) *Cf.* A. Eibner, *Ber.*, **37**, 3605 (1904). M. Q. Doja, *Chem. Reviews*, **11**, 278 (1932), states: "A methyl group in a quinoline ring is known to lose its power of condensation with ketones or aldehydes when the ring is partially or wholly reduced."

(5) C. F. Mabery and L. G. Wesson, THIS JOURNAL, **42**, 1026 (1920).

sulfuric acid and the resulting 16 fractions were precipitated with a hot solution of picric acid in water or alcohol.

No.	H_2SO_4, cc.	G. picric acid		No.	H_2SO_4, cc.	G. picric acid	
		In H_2O	In alc.			In H_2O	In alc.
	Batch I				Batch III		
1	200	2	..	1	200	2	0
2	200	42	25	2	250	62	25
3	200	42	10	3	300	62	20
4	100	17	..	4	300	42	10
	Batch II				Batch IV		
1	200	2	0	1	150	2	0
2	250	52	25	2	200	42	0
3	300	52	20	3	250	62	10
4	300	42	0	4	250	21	0

All the picrates obtained from acid extracts 2, 3 and 4 of each batch were subjected to fractional crystallization from 95% alcohol, until crystalline products were obtained. Next a number of melting points and mixed melting points were made as controls on the seven fractions of picrate mixtures most insoluble in alcohol. Three serial numbers are employed in listing below these picrates; the first number indicates the distillation fraction, the second the acid extraction, and the third the picrate precipitation; *e. g.*, "231" applies to the product that came from the first picrate precipitation of the third acid extract of distillation fraction II. "A" refers to initial melting point of picrates and "B" to the melting point after one recrystallization from alcohol.

Melting Points (uncorr.), °C.

Picrate fractions	M. p. A	M. p. B
231	163–164	163–164
241	142–143	159–160
331	162–165	165–166
341	145–147	160–161
342	145–158	160–161
431	144–145	159–161
441	145–146	160–161

Mixed Melting Points (uncorr.), °C.

Mixed picrate fraction	M. p. A	M. p. B
231 + 331	163.5–164.5	163.5–165
231 + 241	119–123	119–122
331 + 341	123–124	132–133
341 + 441	146–146.5	159.5–160.5
241 + 341	145.5–146	160–160.5
431 + 441	145.5–146	160.5–161
341 + 342	144–146	160–161
342 + 441	144–146	160–161
331 + 431	120–132	120–126

Preliminary experiments had disclosed that, where samples of two mixed picrates had an initial m. p. of 144–146.5° and, after recrystallization from alcohol, a m. p. of 159.5–161°, the $C_{13}H_{21}N$ base was present in high concentration. Accordingly picrates 241, 341, 342, 431 and 441 were combined and recrystallized from alcohol, and then from benzene. From 50 g. of pure picrate with m. p. 158.7°, 21.5 g. of the $C_{13}H_{21}N$ base was separated with ammonium hydroxide. From the reworked residues two other picrates, one of m. p. 115–118° and the other of m. p. 160°, were obtained but were not further investigated. No doubt the Perrin–Bailey method of cumulative extraction, which was perfected toward the close of the present investigation, will prove of service in developing the most practical procedure in isolation of the several bases in this temperature range.

Properties of the $C_{13}H_{21}N$ Base.—It is a colorless oil, with a faint basic but not unpleasant odor, insoluble in water and miscible in all proportions with the common organic solvents. The following physical constants were determined: m. p. 24.5°; b. p. 225.6° at 750 mm.; d_4^{20} 0.8700; n_D^{25} 1.4833 and n_D^{30} 1.4811.

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.61; H, 10.98; N, 7.34. Found: C, 81.40; H, 11.03; N, 7.49. *Mol. wt.* Subs., 10.454 mg.; camphor, 206.452 mg.; Δt, 10.5°. Calcd. for $C_{13}H_{21}N$: mol. wt., 191; found: mol. wt., 185.

An attempt to prepare the methiodide by heating 0.5 cc. of base with 2 cc. of methyl iodide in a sealed tube for thirty hours at water-bath temperature gave a negative result. The base and phthalic anhydride, heated for four hours at 200°, did not react. Reduction experiments with the use of Adams catalyst were unsuccessful. In chloroform solution the base does not react with bromine even on warming, and it can be distilled over heated zinc dust unchanged. The base shows an unusual stability toward alkaline permanganate. In contrast to its stability in alkaline solution, the $C_{13}H_{21}N$ base in 1:5 sulfuric acid reduces permanganate readily. An attempt to effect nitration, in accordance with the procedure of Markownikoff for nitration of methylcyclopentane,[6] ended in failure.

Picrate.—This salt separates on addition of picric acid in water or alcohol to a solution of the acid sulfate and can be crystallized from benzene in yellow needles melting at 158.7°. It is readily soluble in alcohol, 50% acetic acid, acetone and ethyl acetate and only slightly soluble in water, ether and petroleum ether.

Anal. Calcd. for $C_{19}H_{24}O_7N$: C, 54.29; H, 5.71; N, 13.33. Found: C, 54.53; H, 5.61; N, 13.55.

Mercuric Chloride Salt.—This salt, prepared by addition of a solution of mercuric chloride to the base in dilute hydrochloric acid, is difficultly soluble in water and can be crystallized from alcohol in prisms melting at 131.6°.

Anal. Calcd. for $C_{13}H_{21}N \cdot HCl \cdot HgCl_2$, H_2O: N, 2.71; Cl, 20.60. Found: N, 2.85, 2.71; Cl, 20.64.

Chloroplatinate.—The chloroplatinate, prepared in dilute hydrochloric acid solution, crystallizes from dilute alcohol in well-defined rectangular plates, of an orange color and melting with decomposition at 205°. It is only moderately soluble in water and alcohol.

Anal. Calcd. for $C_{13}H_{21}N \cdot H_2PtCl_6$: Pt, 24.65; N, 3.45. Found: Pt, 24.32; N, 3.48.

Acid Sulfate.—This salt crystallizes out on dissolving the base in the calculated amount of sulfuric acid. It is very soluble in water and alcohol, difficultly soluble in ethyl acetate and can be crystallized from acetone in cubes melting at 155°.

Anal. Calcd. for $C_{13}H_{21}N \cdot H_2SO_4$: N, 4.84. Found: N, 4.82.

Experimental Part. II

The $C_{16}H_{25}N$ Base.—The $C_{16}H_{25}N$ base used in the following experiments was isolated from distillation fractions of kero bases, boiling in the temperature zone around 275°, by employment of the Perrin–Bailey cumulative extraction process.[7]

Phthalone.—The base and phthalic anhydride in molecular proportions are heated at 200° for four hours, the melt is dissolved in 15 cc. of concentrated sulfuric acid for each 10 cc. of base used, and the solution is poured onto crushed ice. In final purification the product is crystallized from 95% alcohol in thin rectangular plates, of a deep yellow color and melting at 208°. It dissolves readily in boiling glacial acetic acid, is more difficultly soluble in 95% alcohol, 50% acetic acid and ethyl acetate and is practically insoluble in water and dilute mineral acids. Like quinoline yellow, it sublimes undecomposed at 220° and 45 mm. Treated with sodium ethylate, it separates from alcohol in the form of a crystalline deep orange colored salt which hydrolyzes in water.

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(6) Markownikoff, *Ann.*, **307**, 352 (1899).

(7) See Paper IV of this series by Perrin and Bailey.

In all attempts to hydrolyze the phthalone with dilute sulfuric acid and alcoholic potassium hydroxide, it was recovered unchanged. In oxidation experiments only gums were obtained, from which no crystalline product containing nitrogen was isolated. Unlike quinoline yellow, the new phthalone cannot serve as a spirit-soluble dye and, furthermore, sulfonation experiments ended in failure.

Anal. Calcd. for $C_{24}H_{27}O_2N$: C, 79.77; H, 7.48; N, 3.88. Found: C, 79.75; H, 7.31; N, 3.75. *Mol. wt.* Subs., 0.1008 g.; camphor, 1.060 g.; Δt, 11°. Calcd. for $C_{24}H_{27}O_2N$: mol. wt., 361. Found: mol. wt., 316.

Attempt to Condense Methylcyclopentane with Phthalic Anhydride.—It was of some interest to determine whether a hydrocarbon of naphthenic structure would condense, like the naphthenic base, with phthalic anhydride. However, all attempts to condense methylcyclopentane with phthalic anhydride,[8] with and without the use of zinc chloride, were unavailing.

Hydrochloride of the Dibenzal Compound.—Five grams of base, 6.5 g. of benzaldehyde and 0.5 g. of zinc chloride are heated for eighteen hours in a sealed tube at 190–210°. The viscous reaction product dissolved in ether is precipitated as the hydrochloride (9 g.) by shaking the solution with dilute hydrochloric acid. After being washed with ether and acetone, it crystallizes from a mixture of alcohol and chloroform in long flat prisms, with pyramidal end faces and melting at 241–242°.

Anal. Calcd. for $C_{30}H_{34}NCl$: N, 3.16. Found: N, 2.98.

Dibenzal Compound.—This substance, freed from the hydrochloride with ammonium hydroxide, is insoluble in water and separates from alcohol in ill-defined crystals melting at 120–121°. In chloroform it absorbs an amount of bromine corresponding to two double bonds. It is very resistant to alkaline permanganate.

Anal. Calcd. for $C_{30}H_{33}N$: C, 88.45; H, 8.11; N, 3.44. Found: C, 88.37; H, 7.83; N, 3.71. *Mol. wt.* Subs., 9.187 mg.; camphor, 77.2 mg.; Δt, 11.9°. Calcd. for $C_{30}H_{33}N$: mol. wt., 407. Found: mol. wt., 400.

Picrate of the Dibenzal Compound.—On addition of an alcoholic solution of picric acid to the hydrochloride in chloroform, a granular product, highly insoluble in water and the common organic solvents, separates. It crystallizes from a mixture of alcohol and chloroform in microscopic long flat prisms, with pyramidal end faces and melting at 249–250° with decomposition.

Anal. Calcd. for $C_{36}H_{36}O_7N_4$: C, 67.92; H, 5.66; N, 8.81. Found: C, 67.52; H, 5.41; N, 8.60.

Summary

This paper describes a non-aromatic base of the constitution $C_{13}H_{21}N$ occurring in the crude kerosene distillation of California petroleum.

In further study of the previously isolated $C_{16}H_{25}N$ base, the unexpected discovery has been made that it condenses with phthalic anhydride to form a phthalone.

AUSTIN, TEXAS

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[8] We are indebted to Dr. Edward W. Washburn of the U. S. Bureau of Standards for the methyl cyclopentane used in these experiments.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

The Preparation of Pure Triethanolamine (β, β', β''-Trihydroxytriethylamine)

BY FRANK E. E. GERMANN AND ODON S. KNIGHT

Very pure hydrochloride of triethanolamine can be prepared from technical triethanolamine as follows. The triethanolamine, with or without preliminary fractional distillation, is carefully neutralized with concentrated hydrochloric acid at 10 to 15° and a very slight excess of acid, as shown by litmus paper, added. In an hour the pure white crystals that have settled are filtered off with suction, thoroughly washed with 95% ethyl alcohol and dried for an hour at 110°; yield, 70%, based on the amount of triethanolamine present in the original mixture; m. p. 177–178°; Knorr gives 177°. Calculated percentage of chlorine, 19.10; found, 19.05.

The conversion of the hydrochloride into the free base with silver oxide or alcoholic solutions of sodium or barium hydroxide is difficult because of the solubility of the chlorides in triethanolamine or its ethyl alcoholic solution. For instance, using sodium hydroxide, on distilling off the ethyl alcohol, a small amount of the sodium chloride crystals was observed on the bottom of the flask and on attempting to distil the triethanolamine *in vacuo* much decomposition occurred. This observation led us to believe with Knorr[1] that the presence of any appreciable amount of chlorides causes decomposition on distillation.

Since sodium chloride is less soluble in the higher than in the lower alcohols, it was thought possible that isopropyl alcohol might be substituted with advantage for the ethyl alcohol in the saponification of the hydrochloride, provided the hydrochloride itself was sufficiently soluble in it. Measurements showed its solubility to be 1.1 g. per liter in isopropyl alcohol as contrasted with 3.0 g. per liter in ethyl alcohol, both at 65°.

One hundred grams of triethanolamine hydrochloride was then added to 400 cc. of isopropyl alcohol, to which an equivalent quantity of sodium hydroxide, quickly pulverized in a mortar, had been added. This mixture was refluxed for three hours on a water-bath and after standing overnight the precipitated sodium chloride was removed on a suction filter. The isopropyl alcohol was then distilled off at atmospheric pressure, after which the triethanolamine itself distilled over at 194–195° at 10 mm. pressure. A 90% yield of odorless, clear, pale straw-colored oil, specific gravity, 1.1239 at 20/20°, was obtained, which on titration with sulfuric acid showed a purity of 99%. Its nitrogen content determined on nine different samples by the Kjeldahl–Gunning–Arnold method was on the average 9.35% as against 9.39% calculated, with a maximum variation of 0.09%.

BOULDER, COLORADO

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[1] Knorr, *Ber.*, **30**, 909, 1492 (1897).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Addition of Phenols to the Ethylenic Linkage. The Action of Phenols on Alkylene Halides[1]

BY RICHARD A. SMITH AND JOSEPH B. NIEDERL

It has been demonstrated in previous communications that phenolic bodies will add to unsaturated linkages, principally of the ethenoid type, in the presence of sulfuric acid or other cationoid condensing agents. The products generally are substituted phenols or phenyl ethers.[2]

In this report it will be shown that this type of condensation can be extended to unsaturated halides. The three cresols and phenol were condensed with allyl chloride in the presence of sulfuric acid. The products were identified as isopropenylphenols. These products have been resynthesized in several ways: (a) by the condensation of phenols with allyl alcohol,[3] (b) allyl esters,[4] (c) allyl ethers, and[5] (d) by direct rearrangement of the isomeric isopropenyl phenyl ethers.[2]

Two types of condensation are described. The first consists simply in allowing the phenol, the unsaturated halide and sulfuric acid to stand for an appropriate time at room temperature. The reaction rate is very slow. The second type is more rapid; heat is employed and glacial acetic acid is used in the capacity of a diluent to minimize sulfonation.

The experimental results are consistent with the reaction mechanism which has been advanced previously.

Experimental Part

Slow Condensation.—Phenol and the three cresols were condensed by this method. The procedure involved in all four condensations was similar. A mixture of one mole of the phenol, one mole of allyl chloride, and one mole of sulfuric acid was allowed to stand in a flask, protected from moisture by a calcium chloride drying tube, for a period of six months. The condensation products of phenol, *o*- and *p*-cresol were subjected to the same treatment for the isolation of the reaction product. A volume of water twice that of the reactants was added and the whole then neutralized with sodium carbonate. The organic layer which separated was then removed, water washed and dried with anhydrous sodium sulfate. Distillation at atmospheric pressure was used to obtain the final product. The refractive index and density were taken immediately after distillation to avoid possible errors due to polymerization. In the case of *m*-cresol, the condensation product separated as a crystalline solid, and this was merely filtered off and recrystallized. All of the products have been obtained by resynthesis, as has been stated, and the agreement in properties is satisfactory.

At periods during the condensations, the gases evolved were collected in silver nitrate solutions; it was found in each case that a precipitate of silver chloride was formed.

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(1) Presented at the Washington Meeting of the American Chemical Society, 1933.

(2) Niederl and Storch, THIS JOURNAL, **55**, 284 (1933), and references therein cited.

(3) Niederl, Smith and McGreal, *ibid.*, **53**, 3390 (1931).

(4) Adams, M.Sc. Thesis, New York University, 1930.

(5) Storch, M.Sc. Thesis, New York University, 1930.

PHYSICAL CONSTANTS AND ANALYSES OF THE COMPOUNDS PREPARED

Compound and formula	Prepared from	B. p., °C.	Sp. gr.	n_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-Hydroxy-1-isopropenylbenzene,[a] $CH_2=C(CH_3)C_6H_4OH$	Isopropenyl phenyl ether	203–208	1.024_{28}	1.5452_{28}	80.55	80.23	7.52	7.25
	Allyl chloride and phenol	200	1.020_{26}	1.5320_{26}		80.18		8.36
4-Hydroxy-1-methyl-3-isopropenylbenzene,[b] $CH_2=C(CH_3)C_6H_3(CH_3)OH$	Isopropenyl *p*-cresyl ether	222–224	1.012_{24}	1.5362_{24}	81.07	80.73	8.17	8.00
	Allyl chloride and *p*-cresol	225	1.015_{26}	1.5286_{26}		81.31		8.46
2-Hydroxy-1-methyl-5-isopropenylbenzene,[c] $CH_2=C(CH_3)C_6H_3(CH_3)OH$	Isopropenyl *o*-cresyl ether	225–228	1.020_{28}	1.5395_{28}		80.68		8.35
	Allyl chloride and *o*-cresol	225	1.017_{19}	1.5386_{31}		80.74		8.38
3-Hydroxy-1-methyl-4-isopropenylbenzene,[d] $CH_2=C(CH_3)C_6H_3(CH_3)OH$	Isopropenyl *m*-cresyl ether	225	1.026_{25}	1.5402_{25}		81.40		8.38
	Allyl chloride and *m*-cresol	220–225	1.025_{26}	1.5358_{26}		81.43		8.52
1-Hydroxy-2-*m*-cresoxypropane (impure), $CH_2(OH)CH(CH_3)O_6C_6H_4(CH_3)$	Allyl chloride and *m*-cresol	218–220			72.28	73.72	8.43	8.55
2-*m*-Cresoxypropene-1 (impure), $CH_2=C(CH_3)OC_6H_4(CH_3)$	Allyl chloride and *m*-cresol	about 200			81.07	79.35	8.17	8.12
Dimer of 3-hydroxy-1-methyl-4-isopropenyl,[d] benzene,[b] ($C_{10}H_{12}O_2$)	Allyl chloride and *m*-cresol	74 (m. p.)						
Hexabromothymol,[e] $(CH_3)(CHBr_2)CBr(C_6Br_3)OH$	3-Hydroxy-1-methyl-4-isopropenylbenzene	149 (m. p.)						
Pentabromodehydrothymol,[e] $CBr_2=C(CH_3)C_6Br_3(CH_3)OH$	Hexabromothymol	102 (m. p.)						

[a] Béhal and Tiffeneau, *Bull. soc. chim.*, [4] **3**, 315 (1908); Hoering and Baum, Ger. Pat. 208,886 (1909); Fries and Volk, *Ann.*, **379**, 95 (1911); Fries, Gorss, Selbeck and Wicke, *ibid.*, **402**, 306 (1914).

[b] Guillaumin, *Bull. soc. chim.*, [4] **7**, 381 (1910); V. Auwers, *Ann.*, **413**, 304 (1917); Fries, *ibid.*, **372**, 229 (1910).

[c] Zincke, *Ann.*, **400**, 45 (1913).

[d] Fries and Fickewirth, *ibid.*, **362**, (1908); *Ber.*, **41**, 371 (1908); Guillaumin, *Bull. soc. chim.*, [4] **7**, 381 (1910); Hoering and Baum, German Patent 208,886 (1909).

[e] Baeyer and Seuffert, *Ber.*, **34**, 41 (1901); Fries and Fickewirth, *ibid.*, **41**, 371 (1908).

A blank run containing allyl chloride and sulfuric acid under the same experimental conditions did not yield a precipitate of silver chloride.

More Rapid Condensation.—It is possible to carry out the condensation at more elevated temperatures and so greatly decrease the reaction time. The method allows the isolation of the intermediate phenoxy compound in good yields where this is desired. If the reaction mixture be heated for a short time, the primary reaction product will be the ether; further heating increases the amount of the substituted phenol and decreases the relative amount of ether. The substituted phenol alone may be obtained as the final product. The condensation agent is again sulfuric acid; however, where heat is employed it is necessary to use a diluent to prevent sulfonation. Glacial acetic acid is used in this capacity. Equimolar quantities of allyl chloride, *m*-cresol and sulfuric acid (present as 33% of a glacial acetic acid solution) when refluxed for eight hours yielded approximately equal parts of the ether and the substituted phenol with about 30% of the *m*-cresol having reacted. It is advisable to use an excess of allyl chloride as there is some loss due to volatilization. After refluxing, the reactants were thrown upon water; the organic layer which separated was water washed and extracted with ten per cent. caustic potash. The alkali-insoluble portion was dried with anhydrous sodium sulfate and distilled. Analysis indicated the loss of water on distillation.

The alkaline extract was neutralized with 15% hydrochloric acid, the resulting organic liquid layer water washed and dried with anhydrous sodium sulfate. Distillation yielded isopropenyl-*m*-cresol. The hexa- and pentabromo derivatives were made from samples of this compound prepared by both the slow and rapid condensation. The procedure has been given in a former publication.[3]

Summary

The condensation of phenolic type compounds with the ethylenic linkage has been extended to unsaturated halides and the resulting condensation products were identified.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Common Basis of Intramolecular Rearrangements. II.[1] The Dehydration of Di-*tert*-butylcarbinol and the Conversion of the Resulting Nonenes to Trimethylethylene and Isobutylene

BY FRANK C. WHITMORE AND E. E. STAHLY[2]

The older conception of molecular rearrangements as involving primarily the migration of groups (positive, negative or neutral free radicals) has been superseded in this Laboratory by the hypothesis that the metathetical and elimination reactions[1] of organic chemistry which give rise to most rearrangements, involve the following steps: (1) removal of a group with a complete octet of electrons, leaving an atom with six electrons. The ensuing changes may include the following: (2a) union with a negative ion to form the "normal" metathetical product; (b) The loss of a proton with the formation of a double bond. (c) The atom with only a sextet of electrons may take an electron pair from an adjacent atom, leaving that atom with only six electrons. The group originally held by the electron pair migrates with it. This hypothesis does not assume that a group leaves one part of the molecule and later attaches itself to a different part.[3] The important process is the transfer of an electron pair from an adjacent atom. (3) The *rearranged* fragment from 2c may undergo the processes in 2a, b, c.

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(1) Whitmore, THIS JOURNAL, 54, 3274 (1932).

(2) Presented in partial fulfilment of the requirements for the Ph.D. degree.

Since the important process is the satisfying of the electronically deficient atom, change (2c) might consist of the shift of an electron pair without carrying along its organic group. The latter would thus leave as a positive fragment in much the way that a positive proton leaves the molecule in (2b). The type of organic group most likely to part with an electron pair and become positive would be a tertiary group as evidenced by the striking difference in the action of acids on tertiary alcohols as contrasted with primary and secondary alcohols.

The compounds most likely to give such a splitting of the C–C linkage would thus be those capable of forming a fragment, $R_3C—C—C^{\oplus}$. Substances of this type are practically unknown and their synthesis is difficult. For some time, however, experiments along this line have been in progress in this Laboratory. The results have been complex in the extreme.[4] We have now found one case which gives definite results. It is the dehydration of di-*tert*-butylcarbinol at 180° to give a 77% yield of trimethylethylene. The other products are a small amount of isobutylene and a complex mixture containing some nonenes, a large amount of diisobutylenes and smaller amounts of diamylenes, triisobutylenes and tetraisobutylenes. Dehydration of the carbinol at 155° gives nonenes in 71% yield. Treatment of the nonenes with the dehydrating agent at 200° produces isobutylene, trimethylethylene, and polymers in yields of 50, 68 and 39%, respectively, thus accounting for 98% of the nonenes used.

The possible changes,[1] starting with di-*tert*-butylcarbinol, are as follows: (1) removal of the hydroxyl to give a positive di-*tert*-butylcarbinyl group. This is doubly a positive neopentyl system and consequently most susceptible to rearrangement.[5] No other change is probable.

(2) The transfer of an electron pair with any one of the six methyl groups to give the fragment, $(CH_3)_3C—CH(CH_3)—C^{\oplus}(CH_3)_2$. (A.)

(3*a*) Fragment A would be expected to lose a proton from the tertiary hydrogen or from one of the two methyl groups. The expected nonenes are formed in only small amounts, however, unless dehydration is carried out under the mildest possible conditions.

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[3] *Cf.* Wallis, THIS JOURNAL, **55**, 1702 (1933).

[4] Unpublished work of A. H. Homeyer, S. N. Wrenn, E. E. Stahly, A. L. Houk and J. W. Heyd.

[5] *Cf.* Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932); **55**, 1106 (1933).

(*b*) Another possible change would result in the transfer of the tertiary butyl group to give the fragment, $^{\oplus}CH(CH_3)—C(CH_3)_2—C(CH_3)_3$. No product corresponding to this fragment has been found.

(*c*) The change in fragment A, formed either from the carbinol or *by the addition of a proton to one of the nonenes,* which agrees with the experimental facts is *the transfer of the electron pair from the tertiary butyl group but without the transfer of that group*

$$(CH_3)_3C—CH(CH_3)—C^{\oplus}(CH_3)_2 \longrightarrow (CH_3)_3C^{\oplus} + CH_3CH{=}C(CH_3)_2$$

The positive tertiary butyl fragment gives isobutylene and its polymers. Part of the trimethylethylene is polymerized.

The significance of the apparent instability of the grouping, $R_3C—C—C^{\oplus}$, is being further studied especially in relation to the depolymerization of polymerized olefins.

Experimental

Distillation Equipment.—All of the columns were of the total condensation, adjustable take-off, adiabatic type.[6] The packed sections were as follows: column A, 73 × 2.3 cm.; column B, 65 × 2.5 cm.; column C, 40 × 1.3 cm.; column D, 40 × 1.3 cm.; column E, 25 × 1.0 cm. A, B and C were packed with glass tubes, 5 × 5 mm., and D and E were packed with glass helices.[7]

General.—Di-*tert*-butylcarbinol was prepared by reducing hexamethylacetone which was made by the sodamide synthesis[8] from diisopropyl ketone.

Preparation of Diisopropyl Ketone.—Oxidation of diisopropylcarbinol with sulfuric acid–sodium dichromate mixture below 35° gave a 74% yield of diisopropyl ketone,[9] b. p. 120–125° (742 mm.), n^{20}_{D} 1.4001.

Hexamethylacetone.—A typical preparation will be described.[9] Toluene was distilled through Column A and the fraction distilling at 110–110.5° (740 mm.) was dried over sodium. Three liters of this toluene was placed in a 5-liter 3-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. Commercial sodamide (about 50%) was pulverized under toluene and 160 g. (2 moles) was suspended in the toluene. To this suspension was added 228 g. (2 moles) of diisopropyl ketone. The mixture was stirred vigorously while heating to brisk reflux in an oil-bath. When the evolution of ammonia ceased the solution was cooled and 270 g. of methyl sulfate (2.14 moles) was added during one hour. When the refluxing again ceased the mixture was heated to boiling for fifteen minutes and then allowed to cool. To the cold solution 400 cc. of water and 200 cc. of ammonium hydroxide were added during two hours and stirring continued for twelve hours. Vigorous stirring was necessary throughout the whole process. The upper layer was then separated and washed with 5% hydrochloric acid and 5% sodium carbonate solution successively. The main portion of toluene was distilled off and the remainder used in the next step. Some of the pentamethylacetone was purified by distillation through Column A: b. p. 132–134.5° (730 mm.); n^{20}_{D} 1.4073.

The combined crude products from methylation of 5 moles of diisopropyl ketone were methylated in 3 liters of toluene as above. Distillation of the final toluene solution through Column B gave 374 g. of hexamethylacetone, b. p. 144–50° (740 mm.) n^{20}_{D} 1.4191–1.4197; yield, based on diisopropyl ketone, 52%. It was identified by con-

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(6) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(7) Wilson, Laughlin and Parker, *ibid.*, **55**, 2795 (1933).

(8) Haller and Bauer, *Ann. chim.*, [8] **29**, 313 (1913).

(9) Whitmore and Laughlin, THIS JOURNAL, **54**, 4392 (1932).

version to methyl-di-*tert*-butylcarbinol by reaction with methylmagnesium chloride;[10] m. p. of carbinol, 42°.

Reduction of Hexamethylacetone.—The reduction was by the method of Krueger.[11] From 4 half-mole runs, 220 g. (76% yield) of solid carbinol, b. p. 108–113° (150 mm.), was obtained. Redistillation through Column D gave 198 g., b. p. 117–118° (166 mm.), m. p. 50–51°.

Dehydration of Di-*tert*-butylcarbinol.—In a typical dehydration 57.7 g. (1 mol) of carbinol and 2 g. (0.02 mol) of 1-chloro-4-naphthalenesulfonic acid[12] were placed in a 200-cc. flask attached to Column D. The take-off tube was attached to a copper coil condenser cooled with water at 10°. The receiver was cooled in an ice-bath and its outlet was connected to a gas collector containing saturated salt solution. The flask was heated in an oil-bath at 180°. Dehydration proceeded without *evolution of gas* until almost the theoretical amount of water had been drawn off (three hours). At this point the distillation temperature dropped from 88 to 34° (733 mm.), trimethylethylene distilled, and gas was evolved. After one and one-half hours the distillation temperature rose and the evolution of gas ceased. The receiver was changed and distillation was continued under reduced pressure to give 16.1 g. of material, b. p. 43° (737 mm.) to 132° (113 mm.) and a residue consisting of 6 g. of liquid and 2 g. of solid material. A total of 90% of the starting material was accounted for as follows: water, 6.2 g. (theory, 7.2); gas, 1.2 liters, trimethylethylene 21.4 g. (calcd. 28 g., yield 77%) 22.1 g. of high boiling material (polymers).

Identification of Trimethylethylene.—The above volatile olefin, b. p. 34° (733 mm.), n^{20}_{D} 1.3815, was identified by conversion to the dibromide and hydrolysis to methyl isopropyl ketone by refluxing with water.[13] After the small bromide layer had disappeared and an upper one formed, the ketone was distilled through Column E and the 2,4-dinitrophenylhydrazone prepared, m. p. 116–118°. Two crystallizations raised the m. p. to 117–118°. Starting with pure trimethylethylene obtained by fractionation of the olefins from pure *tert*-amyl alcohol, a similar series of transformations yielded a 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 117–118°, thus proving the olefin from di-*tert*-butylcarbinol to be trimethylethylene.

Higher-Boiling Olefins.—The olefins obtained from three similar dehydrations were combined and distilled through Column D; 21 cuts (0.5–2.0 g. each) were taken from 82° (742 mm.) to 161° (730 mm.) and sixteen similar cuts between 116° (182 mm.) and 141° (75 mm.). All fractions decolorized dilute carbon tetrachloride solutions of bromine. A curve obtained by plotting n^{20}_{D} against total distillate gave six small breaks in an otherwise steadily rising curve. A molecular weight determination was made for the fraction corresponding to each of these breaks. For the four higher boiling fractions Solty's modification of Rast's camphor method was used.[14] It was not satisfactory for the two more volatile samples because vaporization caused a serious error. The lowering of the freezing point of benzene was used in the usual manner for the latter two.

The cuts corresponding to the breaks and the b. p., n^{20}_{D}, and molecular weight of each follow: 5–8, 4.6 g., 101–119° (740), 1.415, 118; 11–13, 5.1 g., 125–132° (742), 1.423, 124; 18–20, 2.3 g., 142–151° (738), 1.430, 1.40; 23–26, 5.0 g., 159° (736)–122° (130), 1.436, 147; 30–31, 1.8 g., 127–131° (102), 1.440, 172; 32–33, 2.6 g., 131–132° (102), 1.441, 172. The fractions thus correspond in properties and molecular weights to nonenes, diamylenes, and triisobutylenes. Although there was no break in the curve for 35–36, the refractive index corresponded to that for the ordinary mixture of the tetraisobutylenes, n^{20}_{D} 1.452.[15]

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[10] Whitmore and Laughlin, THIS JOURNAL, 55, 3736 (1933).

[11] *Cf.* Whitmore and Krueger, *ibid.*, 55, 1531 (1933).

[12] Prepared by F. A. Karnatz of this Laboratory.

[13] Whitmore and co-workers, THIS JOURNAL, 55, 1136 (1933).

[14] "Quant. Org. Micro. Analysis," P. Blakiston's Son and Co., New York, 1930, p. 219.

Analysis of the Gases.—An Orsat apparatus was used with 100-cc. samples of the gas (25°). Carbon dioxide was absorbed by 40% potassium hydroxide, oxygen by potassium pyrogallate solution, and isobutylene by 68% sulfuric acid,[16] other olefins by bromine water, and carbon monoxide by cuprous chloride in hydrochloric acid solution. Remaining gas was considered to be nitrogen as it was nearly four times the amount of oxygen. The average of three analyses gave the composition of the gas as 1% carbon dioxide, 29.7% isobutylene, 0.2% other olefins, 0.2% carbon monoxide and 69% air. Thus the total volume of gas, 1200 cc., corresponded to 0.9 g. of isobutylene, a yield of 4%.

Summary of Products.—The dehydration of 57.7 g. of di-*tert*-butylcarbinol at 180° gave the following: water, 6.2 g. (86%), trimethylethylene, 21.4 g. (77%), isobutylene, 0.9 g. (4%) and polymers, 22.1 g. (42%).

Dehydration of the Carbinol at Lower Temperature without Splitting.—The dehydration of 43 g. of di-*tert*-butylcarbinol by 1.5 g. of 1-chloro-4-naphthalenesulfonic acid was conducted below 155°. The water formed was not drawn off but allowed to reflux in the column. After two and one-half hours the bath was removed and the pot cooled. The olefins were shaken with 30 cc. of 10% sodium hydroxide solution and extracted with ether. The ether solution after drying over sodium was distilled through Column D. The main fractions of the olefins, 18.6 g., 71% yield, distilled 123–140° (733 mm.) and had n^{20}_{D} 1.4230–1.4262. A residue of unchanged carbinol of 13 g. remained, m. p. and mixed m. p. 42–45°.

Splitting of the Nonenes Obtained from Di-*tert*-butylcarbinol.—To 18.5 g. of the nonenes was added 0.4 g. of 1-chloro-4-naphthalenesulfonic acid and the flask attached to Column D and heated as in the dehydration. Upon heating the bath to 145–205°, gas was evolved and trimethylethylene distilled. The total products obtained were: 2300 cc. of gas (27°), 7.0 g. of trimethylethylene, b. p. 34–36°, n^{20}_{D} 1.3800, 7.2 g. of yellow liquid residue, n^{20}_{D} 1.4350; total products recovered, 18.3 g. (98%). Analysis of the gas with an Orsat apparatus showed it to contain 73.1% isobutylene and 3% trimethylethylene or 3.9 g. and 0.2 g., respectively. The nonenes were thus split to yield 68% trimethylethylene, 50% isobutylene and 39% polymers.

Summary

1. Di-*tert*-butylcarbinol has been dehydrated to give a 77% yield of trimethylethylene together with isobutylene and its polymers.

2. The dehydration has been shown to proceed by way of nonenes which are unstable at 180–200° in the presence of the dehydrating agent.

3. These unusual reactions are interpreted in terms of the current theory of molecular rearrangements.

4. This type of reaction is being further studied.

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(15) Unpublished results of S. N. Wrenn of this Laboratory.

(16) Marcowitch and Moore, *Nat. Pet. News*, Oct. 14 and 21, 1931.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Effect of Traces of Carbon Disulfide on the Yields of Grignard Reagents[1]

BY FRANK C. WHITMORE AND DARWIN E. BADERTSCHER[2]

The preparations of many of the compounds needed for researches in progress in this Laboratory involve the use of Grignard reagents. Inasmuch as maximum yields are desirable it seemed worth while to investigate means of increasing the yields of Grignard reagents.

The effect of added substances and also of other factors, such as speed of addition and concentration of halide, has been studied by several workers.[3] A decreased yield of alkyl Grignard reagent usually is accompanied by an increase in the amount of olefin which is formed, apparently by the removal of hydrogen halide from the halide molecule by the magnesium. In acid pickling baths for removal of the surface oxide from iron and steel it is customary to add small amounts of so-called inhibitors which, while they do not interfere with oxide removal, do check the action of the acid on the metal itself. Rhodes and Kuhn[4] have made a careful study of these inhibitors and find certain cyclic nitrogen compounds to be the most effective. Consequently the effect of traces of pyridine, acridine, and α-picoline on the yield of *tert*-butyl- and *tert*-amylmagnesium chlorides was studied. In no case was the yield of Grignard reagent raised appreciably by traces of the inhibitors. Larger amounts of inhibitor delayed the reactions and decreased the yields. Thus the inhibiting action extended to the formation of the Grignard reagent as well as to the formation of hydrogen by the action of magnesium.

Freundler and Damond[5] noticed in the preparation of *sec*-butylmagnesium bromide that when a certain lot of ether was used the yield of Grignard reagent was increased and the amount of olefin formed was decreased. On careful investigation they found that this particular lot of ether had a small amount of carbon disulfide present as an impurity.

This lead looked promising and has been investigated in a quantitative manner. Traces of carbon disulfide present during its preparation raise the yield of Grignard reagent from primary and secondary bromides and iodides. The increase in yield is greatest in the more concentrated halide–ether solutions (compare Tables I and II). The increase in yield is accompanied by a marked decrease in the total volume of gas evolved (Table

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[1] Presented before the Organic Division, A. C. S., March 28, 1933.

[2] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[3] Tschelinzeff, *Ber.*, **38**, 3664 (1905); **39**, 773 (1906); Hepworth, *J. Chem. Soc.*, **119**, 1249 (1921); Gilman and co-workers, THIS JOURNAL, **51**, 1583 (1929); *Rec. trav. chim.*, **46**, 463 (1927); Johnson and Adkins, THIS JOURNAL, **53**, 1520 (1931).

[4] Rhodes and Kuhn, *Ind. Eng. Chem.*, **21**, 1066 (1929).

[5] Freundler and Damond, *Bull. soc. chim.*, [3] **35**, 108 (1906).

II). The exact composition of these gases, with and without carbon disulfide present, is being studied at the present time. *tert*-Butyl bromide gave erratic results. Primary, secondary and tertiary chlorides are being investigated. The chlorides appear to be rather sensitive to traces of carbon disulfide, small amounts being sufficient to completely stop the reaction. The violence of the reaction between the halide and magnesium is in all cases moderated when carbon disulfide is present.

In each case in which the Grignard reagent was prepared in the presence of a trace of carbon disulfide the yield of product prepared from the reagent and the carbonyl compound was higher, based not only on halide, *but also on Grignard reagent*, than when the reagent was prepared in the absence of carbon disulfide (see Table II). This phenomenon is being studied further with the purpose of investigating the effect of traces of carbon disulfide on the reducing, coupling and enolizing action of the Grignard reagent.

In all cases in which carbon disulfide was present the solution became jet black, due to the presence of a small amount of very finely divided black solid, the nature of which has not been investigated.

Other workers in this Laboratory have fully confirmed our results.

Experimental

The results are listed in Tables I and II. Only a few details need be noted. In the larger runs, it was found advisable to start the reaction with a small amount of a concentrated solution (about 1:1) of halide in *pure* ether because the carbon disulfide, while it raises the yield, retards the start of the reaction. The carbon disulfide is then added to the remainder of the halide–ether solution, once reaction is started.

TABLE I

Halide	Ratio CS_2 to ether by vol.	Yield of RMgX, % CS_2 present	 No CS_2 present
Isopropyl bromide	1:500	No reaction	82.5
	1:1000	87.9	
	1:2500	81.5	65.1
	1:2500	84.3	74.0
	1:4000	88.3	
Isobutyl bromide	1:4000	86.8	81.7
	1:4000	88.5	83.2
sec-Butyl bromide	1:4000	84.8	78.2
Capryl bromide	1:600	No reaction	67.0
	1:4000	71.2	66.0
sec-Butyl chloride	1:600	No reaction	87.2
	1:4000	79.6[a]	87.3
tert-Butyl bromide[b]	1:4000	40.6	38.9
	1:4000	44.5	43.3

[a] Reaction hard to start and did not proceed smoothly.

[b] Further experiments with *tert*-butyl bromide gave erratic results with poor checks.

TABLE II (LARGER RUNS)

ISOPROPYL BROMIDE; PREPARATION OF METHYL ISOPROPYL CARBINOL

Size of runs, 0.75 mole. Vol. of ether used, 250 cc. 0.1 cc. of CS_2 used in each run in which CS_2 was present.

	CS_2 present			No CS_2	
Yield of RMgX, %	89.6	97.0	89.3	64.4	56.5
Gas evolved, liters	2.9	1.1	0.7	4.7	6.9
Yield of carbinol, %					
Based on halide	48.0	61.7		29.3	20.0
Based on Grignard		63.4			34.0

n-PROPYL BROMIDE: PREPARATION OF METHYLETHYL-*n*-PROPYLCARBINOL FROM *n*-PROPYLMAGNESIUM BROMIDE AND METHYL ETHYL KETONE

Size of runs, 2.0 moles. Volume of ether used, 500 cc.

	0.25 cc. CS_2	0.4 cc. CS_2	No CS_2
Yield of RMgX, %	88.3	88.2	65.5
Gas evolved, liters	3.7	4.6	11.8
Yield of carbinol, %			
Based on halide	70.5	69.0	51.5
Based on RMgX	80.0	78.2	65.5

ISOPROPYL IODIDE

Size of runs, 0.25 mole. Volume of ether used, 90 cc.

	0.1 cc. CS_2	No CS_2
Yield of RMgX, %	79.0	56.0

It appears from the results with *n*-propyl bromide (Table II) that only a trace of carbon disulfide is necessary. There was very little difference in the yield of *n*-propylmagnesium bromide when 0.25 cc. and 0.4 cc. of carbon disulfide was present.

The reactions in Table I were carried out using 0.05 mole of halide and 30 cc. of ether in each.

The reactions were carried out in all-glass apparatus, two reactions being carried out at once, one with and one without carbon disulfide. The reactions given in Table II were carried out with larger amounts as indicated.

Summary

1. "Pickling" inhibitors do not increase the yield of Grignard reagents.
2. Traces of carbon disulfide raise the yield in the preparation of the Grignard reagents from several aliphatic primary and secondary bromides and isopropyl iodide. Chlorides are being studied at the present time.
3. The increase in yield is accompanied by a decrease in the volume of gas evolved during the preparation of the Grignard reagent.
4. Preliminary experiments indicate that the yield of product prepared from the Grignard reagent and a carbonyl compound is higher, based on Grignard reagent, when the reagent was prepared in the presence of a trace of carbon disulfide. This work is being continued.

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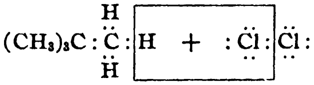
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Preparation and Properties of Neopentyl Chloride in Relation to Molecular Rearrangements[1]

BY FRANK C. WHITMORE AND GEO. H. FLEMING[2]

Tissier[3] and Richard[4] prepared what appeared to be neopentyl chloride. The former stated that the monochloride obtained by the chlorination of neopentane was identical with that obtained from neopentyl alcohol and dry hydrogen chloride and that it decomposed on distillation. It has recently been found in this Laboratory that neopentyl chloride cannot be prepared from the alcohol.[5] In the present study it has been found that neopentyl chloride, formed by the chlorination of neopentane, is stable at 200° for long periods of time and is extraordinarily inactive, giving none of the ordinary reactions of alkyl halides except the formation of a Grignard reagent. Through that reaction and the action of phenyl isocyanate, it has been converted to *tert*-butylacetanilide, thus showing that it forms a Grignard reagent without rearrangement.[6]

The failure to obtain neopentyl chloride from neopentyl alcohol and its successful preparation from neopentane by chlorination illustrate again the instability of the "positive" neopentyl group and the stability of the same group when "negative."[7] The latter also confirms the common conception that chlorination involves the entrance of "positive" chlorine into the molecule. Thus the formation of neopentyl chloride may be represented electronically as involving the change:



$$(CH_3)_3C:\underset{\displaystyle H}{\overset{\displaystyle H}{\ddot{\underset{\cdot\cdot}{C}}}}:\boxed{H\ +\ :\ddot{\underset{\cdot\cdot}{Cl}}:}\,\ddot{\underset{\cdot\cdot}{Cl}}:$$

in which the neopentyl group is not deprived of any of its electrons. The stability and inactivity of neopentyl chloride are strong indications of the tenacity with which the neopentyl group holds its electrons. The "electronegativity" of this group is being studied in a variety of ways in this Laboratory.

Experimental

Chlorination of Neopentane.—The reaction of neopentane and chlorine in direct sunlight at room temperature is extremely vigorous, much heat is evolved and there is some charring. With the light of a 1000-watt tungsten lamp, the chlorination takes place more slowly.

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(1) *Cf.* THIS JOURNAL, **54**, 3460 (1932); **55**, 3403 (1933).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Tissier, *Ann. chim. phys.*, [6] **29**, 344 (1893).

(4) Richard, *ibid.*, [8] **21**, 323 (1910).

(5) Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932).

(6) *Cf.* Whitmore and Lux, *ibid.*, **54**, 3448 (1932).

(7) *Cf.* Whitmore and Homeyer, *ibid.*, **54**, 3436 (1932).

Neopentane was chlorinated by passing chlorine over the surface of the hydrocarbon at 0° in diffused daylight. After distillation of a small sample of the crude chloride had shown it to be stable, the main fraction was distilled at atmospheric pressure through a precision column.[6] *No tertiary amyl chloride was formed during the chlorination or the distillation.*

Pure neopentyl chloride has the following physical constants: d_4^{20} 0.866; n_D^{20} 1.4042; f. p. $-20 \pm 1°$; mol. ref. 30.01, calcd. 30.06; b. p. (Cottrell) 84.4° (760 mm.), 83.9° (750 mm.), 83.5° (740 mm.).

Reactivity of Neopentyl Chloride

Formation of Grignard Reagent.—Neopentyl chloride in dilute ether solution reacts slowly with magnesium. The product with phenyl isocyanate gives an anilide, m. p. 125–126°. A known sample of *tert*-butylacetanilide had m. p. 131° and mixed m. p. 126–128°, showing that the conversion of the chloride to the Grignard reagent involved no rearrangement. The Grignard solution with mercuric chloride gives neopentylmercuric chloride, m. p. 116.5–117°.[8]

Magnesium without Solvent.—*n*-Amyl chloride reacts completely with magnesium in eighteen hours at 200°, whereas neopentyl chloride was recovered unchanged after seventy hours under the same conditions.

Silver Acetate in Ether.—Contrary to the results of Tissier,[3] neopentyl chloride failed to react when heated for six hours at 40° and twelve hours at 60°.

Other Reagents.—While *n*-amyl chloride reacts completely with alcoholic potash in one hour at 100°, neopentyl chloride remained unchanged at the end of twenty hours under the same conditions. The chloride failed to react with cuprous cyanide in a sealed tube at 90° during two hundred hours. While *n*-amyl chloride reacts with potassium iodide in acetone to the extent of about 33%, neopentyl chloride gives no reaction under the same conditions.[9] The chloride failed to react with potassium acetate in absolute ethyl alcohol at 125° during thirty hours. Neither *n*-amyl nor neopentyl chloride reacted appreciably with diphenylmercury at 125° during seventeen hours. The former reacted slightly more than the latter when heated at 200°.

The other neopentyl halides are being prepared and studied in this Laboratory.

Summary

1. Neopentyl chloride has been obtained by direct chlorination of the corresponding hydrocarbon.
2. The physical constants of this chloride have been determined.
3. Neopentyl chloride has been found to be very stable and inactive chemically. The Grignard reagent has been formed.

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[8] This substance was prepared by E. L. Wittle of this Laboratory.

[9] This reaction is being studied by F. W. Herman.

[CONTRIBUTION FROM THE LABORATORY OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

The Isolation of a Sodium Sulfuric Acid Ester of Galactan from Irideae Laminarioides (Rhodophyceae)

BY W. Z. HASSID

Several investigators,[1] working on marine algae reported ethereal sulfates in these plants. However, in no case was the complete structure of these compounds determined with any degree of certainty.

In the present work the writer has isolated from *Irideae laminarioides* a comparatively simple ethereal sulfate, the complete chemical nature of which has been determined.

Extraction.—The plants *Irideae laminarioides* were collected at Moss Beach, California, washed immediately with distilled water, dropped into boiling 95% alcohol and boiled for ten minutes. The plants were brought to the laboratory, the alcohol poured off, the contents ground and extracted in a Soxhlet extractor, first with methyl and then with ethyl alcohol, until free of chlorophyll. The extracted residue was then dried at 50° in a vacuum oven.

Thirty grams of this material was heated with four liters of water on a steam-bath for several hours, until a colloidal solution was formed The solution was filtered on a large Buchner funnel through a silk filter. The residue on the silk filter was taken up with about three liters of water, heated for several hours on the steam-bath and filtered again. The combined filtrates were placed in a large evaporating dish and evaporated to about 800 cc. The solution was then poured into two liters of 90% alcohol. A milky colloidal solution was formed and was allowed to stand for several hours. The clear supernatant solution was decanted from the residue, which settled at the bottom, and concentrated under reduced pressure to about 500 cc. It was then slowly poured with continual stirring into 10 volumes of 95% alcohol, whereupon a precipitate of white flocculent threads formed. After an hour this was filtered and washed, using a silk filter, first with 95% and then with absolute alcohol and finally dried in a vacuum oven at 50°. About 10 g. of a snow white substance was obtained, which did not reduce Fehling's solution. It formed a colloidal solution when dissolved in water. Its specific rotation $[\alpha]_D$ was 69.2 after two reprecipitations from alcohol. When dissolved in water its *P*H was 6.8.

Hydrolysis.—A solution of 10 g. of the dry material in 500 cc. of 2% sulfuric acid was heated under a reflux condenser at a temperature of 105–110° for seven hours, cooled and nearly neutralized with a hot saturated solution of barium hydroxide and completely neutralized with barium carbonate. The mixture was then heated to 80° and allowed to stand overnight, filtered, the precipitate washed with hot water and the filtrate diluted to one liter. Aliquot portions of this were concentrated under reduced pressure. The reducing value of four 10-cc. aliquots was determined in terms of glucose with Fehling's solution, using the Munsen Walker tables. The mean value, when arbitrarily calculated to galactose applying Browne's factor 0.898[2] to the value for glucose, indicated hydrolysis of 54.0%.

Identification of Galactose.—(1) An aliquot representing 2 g. of the prepared ester was evaporated under reduced pressure to a thin sirup. The concentrated solution was treated with a large volume of methyl alcohol and then 1 cc. of glacial acetic acid was added, inoculated with a minute crystal of galactose and allowed to stand for several days. The crystals which deposited in the bottom of the beaker were collected, dissolved in water, and an orange-yellow phenylosazone was prepared. Its melting point was 194–196°. This corresponds to the melting point of the phenylosazone of galactan, given by Mulliken[3] as 196°.

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(1) P. Haas, *Biochem. J.*, **15**, 469 (1921); F. Fairbrother and H. Mastin, *J. Chem. Soc.*, **123**, 1412 (1923); W. F. Hoffman and R. A. Gortner, *J. Biol. Chem.*, **65**, 371 (1925); G. M. Bird and P. Haas, *Biochem. J.*, **25**, 403 (1931); W. L. Nelson and L. H. Cretcher, *J. Biol. Chem.*, **94**, 147 (1931).

(2) C. A. Browne, "Handbook of Sugar Analysis," John Wiley and Sons, New York, 1912, p. 421.

(2) A confirmatory test showed that the phenylosazone could be prepared from the sirupy hydrolyzate without first obtaining the actual galactose crystals.

Quantitative Determination of Galactose.—Van der Haar's modification of the Kent–Tollens–Creydt method[4] with the additional precautions suggested by Wise and Peterson[5] was used for the quantitative determination of galactose. A determination, in triplicate, on the substance under consideration showed 53.2% anhydrogalactose.

Test for Pentose Sugars.—(1) Tollens' phloroglucinol method was applied to the hydrolyzed and unhydrolyzed substance. Both samples gave a yield equivalent to 0.5% of furfural. However, this result was probably due to the hydroxymethylfurfural obtained from the galactose, as it is in fair agreement with the results of Wise and Peterson,[5] who report 0.47% hydroxymethylfurfural due to galactose, and Schorger and Smith,[6] who report 0.55%.

(2) Samples of the hydrolyzed and unhydrolyzed substance were also examined for pentose sugars by the thiobarbituric acid method of Dox and Plaisance.[7] No precipitate of furfural malonyl-thiourea was obtained by the addition of the thiobarbituric acid to the hydrochloric acid distillate.

(3) Attempts were also made to determine whether any pentose or methylpentose sugar was present in the hydrolysis products of the substance, using various phenylhydrazine derivatives. No evidence was obtained for the presence of either pentoses or methylpentoses.

Test for Uronic Acids.—Dore's[8] modification of the Le Fèvre method for determination of uronic acid was applied to this substance. The results were negative.

Determination of the Sodium Ethereal Sulfate Group.—Ignition of the substance in an electric muffle at red heat showed the ash content to be 25.4%. The ash was analyzed for sulfur from the weight of barium sulfate obtained when the ash was dissolved and the sulfate precipitated with barium chloride. The sulfur content was 5.84%.

The original substance was analyzed for its sulfur content in a Parr bomb by oxidation with sodium peroxide and potassium chlorate; 11.5% sulfur was found by this method.

The substance was also hydrolyzed for two hours with 1:4 hydrochloric acid and the products of hydrolysis were examined for sulfur: 12.4% sulfur was found.

Sulfur in the substance by the Parr bomb method	11.5%
Sulfur in the substance by the hydrolysis with hydrochloric acid	12.4%
Sulfur in the ash	5.8%

From the above results it is evident that the sulfur content in the substance is approximately double the quantity of that in the ash.

Tests for sulfate ions were also made by dissolving the substance in warm water and adding barium chloride. There were no sulfate ions present in the solution.

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[3] S. P. Mulliken, "Determination of Pure Organic Compounds," John Wiley and Sons, New York, 1911, Vol. I, p. 30.

[4] A. W. Van der Haar, "Nachweis zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren," Gebrüder Borntraeger, Berlin, 1920, pp. 124–126.

[5] L. E. Wise and F. C. Peterson, *Ind. Eng. Chem.*, **22**, 362 (1930).

[6] A. W. Schorger and D. F. Smith, *ibid.*, **8**, 494 (1916).

[7] A. W. Dox and G. P. Plaisance, THIS JOURNAL, **38**, 2156 (1916).

[8] W. H. Dore, unpublished data.

Fifty-mg. portions of the ash were analyzed for sulfate, calcium, magnesium and sodium: 34.8 mg. of sulfate was found, 13.5 mg. of sodium and 1 mg. each of calcium and magnesium.

These results are in close agreement with the assumption that the ash is chiefly sodium sulfate.

Preparation of the Sulfuric Acid Ester of Galactan.—(1) Two grams of the substance was dissolved in 200 cc. of water and placed in an electrodialysis apparatus described by Greenberg and Greenberg.[9] The electrodialysis proceeded for seventy-two hours. The solution was then concentrated to a small volume and poured into 95% alcohol. The physical appearance of the precipitated substance thus obtained was quite different from that of the original. The fibrous structure had disappeared and the appearance was that of an amorphous granular powder. It gave an acid reaction; its *P*H was 3.6.

(2) Another 2-g. portion of the substance was dissolved in 200 cc. of water, placed in an 800-cc. capacity collodion bag. The bag with the solution was placed in a vessel in which water at 55° was continuously circulating. The dialysis proceeded for seventy-two hours. At the end of that time the solution in the bag was concentrated to a small volume and poured into alcohol as before. The acid ester was obtained as in (1).

Since no pentose sugar and no uronic acid could be found in the isolated substance, galactose appears to be the only sugar present. This conclusion is also supported by the fact that the reducing value corresponding to 54% of the substance, when arbitrarily calculated to galactose, was in satisfactory agreement with the value 53.2% calculated as anhydrogalactose by the modified Van der Haar method.

That the substance is a sodium ethereal sulfate was apparent from the fact that it contained approximately double the quantity of sulfur found in its ash, and from the fact that most of the ash consisted of sodium sulfate.

Comparison of actual results with calculated values, as shown in the table, indicates that there is one unit of galactose in the substance for each sodium ethereal sulfate group.

	Calculated, %	Found, %
Sulfur	12.1	12.0
Carbohydrate portion	54.8	54.0
Sodium ethereal sulfate	45.0	44.7

The table shows a close agreement between the percentages found and percentages calculated for the sulfur content, carbohydrate fraction and the sodium ethereal sulfate group.

Corresponding to the results which have been obtained for various polysaccharides, it might be expected that the structure of this substance is represented by a number of anhydrogalactose units united by glucosidal linkages or oxygen bridges to form chains or rings. The fact that this substance is fibrous strongly suggests that its structure may be a chain rather than a ring structure. Presumably the ethereal sulfate groups exist as side chains formed by replacement of hydroxyl groups. It is impossible of course to determine with certainty the position of the linking oxygen bridges, but assuming that the galactose units possess the usual

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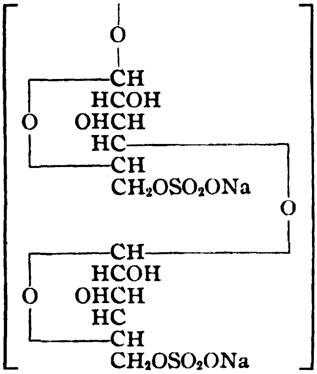
[9] D. M. Greenberg and L. D. Greenberg, *J. Biol. Chem.*, **99**, 1 (1932).

1:5 ring, it is perhaps not unreasonable to propose a chain structure similar to that put forward by Sponsler and Dore[10] for cellulose.

The position of the ethereal sulfate group is in doubt, but one may anticipate that it would be found attached to the sixth C atom. The following consideration upholds the validity of this suggestion: the galactose unit has a 1:5 ring structure, and therefore the group attached to the sixth C atom must protrude from the ring. Owing to the steric position of the groups attached to this atom, they will tend to be more reactive than other groups. Hence the ethereal sulfate group is assigned to the sixth C atom as the most probable position.

In accordance with these ideas the arrangement shown is tentatively proposed showing the linkage between two units.



The polysaccharide itself is made up of an unknown number of these building units, perhaps similarly arranged.

The sulfur in this substance is apparently united with the carbohydrate portion, since it is not precipitated as sulfate when barium chloride is added to an aqueous solution of this substance.

The sodium, however, appears to exist in ionic form, since it moves freely and passes through a collodion membrane when the substance is subjected to electrodialysis or plain dialysis.

The rest of the substance may be considered as a large negatively charged colloidal micelle and does not pass through the membrane.

The writer wishes to acknowledge his indebtedness to Mr. W. H. Dore for the valuable advice received during the course of the experimental work.

Summary

1. A sodium sulfuric acid ester of galactan has been isolated, apparently for the first time, from *Irideae laminarioides*.
2. When subjected to dialysis the sodium was practically all removed from the substance and an acid sulfuric ester of galactan resulted.

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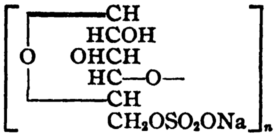
(10) O. L. Sponsler, and W. H. Dore, "Colloid Symposium Monograph," Chemical Catalog Company, Inc., New York, 1926, Vol. IV, p. 174.

3. No sulfur was removed by dialysis.
4. The physical properties of this acid were different from those of the original substance. It had the appearance of an amorphous granular powder in contrast with the fibrous structure of the original substance.
5. A 1% solution of the acid had a *P*H of 3.6.
6. The tentative structural formula shown is proposed for the substance in which *n* is unknown.



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The Synthesis and Reactions of Certain Nitrogen Ring Compounds over Nickel

BY CHARLES F. WINANS AND HOMER ADKINS

In this group of three papers we are surveying the application of nickel as a catalyst for reactions which result in the formation of amines.[1] These reactions are of four general types. In the first type are those in which an amine reacts with an alcohol or amine with the elimination of water or ammonia

$$ROH + RNH_2 \longrightarrow R_2NH + H_2O \quad (I)$$
$$RNH_2 + RNH_2 \longrightarrow R_2NH + NH_3 \quad (II)$$

In the second group a cyano, oximino, nitro or nitroso group is hydrogenated successively to an imine and an amine

$$RC{\equiv}N \xrightarrow{H_2} RCH{=}NH \quad (III)$$
$$R_2C{=}NOH \xrightarrow{H_2} R_2C{=}NH + H_2O \quad (IV)$$
$$RCH{=}NH \xrightarrow{H_2} RCH_2NH_2 \quad (V)$$

In the third group a nitrogen to nitrogen or nitrogen to carbon bond undergoes hydrogenolysis with the formation of amines

$$RCH(N{=}CHR)_2 \xrightarrow{H_2} RCH_2NH_2 + (RCH_2)_2NH \quad (VI)$$
$$RNHNHR \xrightarrow{H_2} 2RNH_2 \quad (VII)$$

In the fourth group an imine, aldehyde or ketone adds an amine, followed in most cases by hydrogenolysis with the elimination of ammonia or water

$$RCH{=}NH + R'NH_2 \longrightarrow RCH(NH_2)NHR \xrightarrow{H_2} RCH(R)NH + NH_3 \quad (VIII)$$
$$RCH{=}O + R'NH_2 \longrightarrow RCH(OH)NHR \xrightarrow{H_2} RCH(R)NH + H_2O \quad (IX)$$

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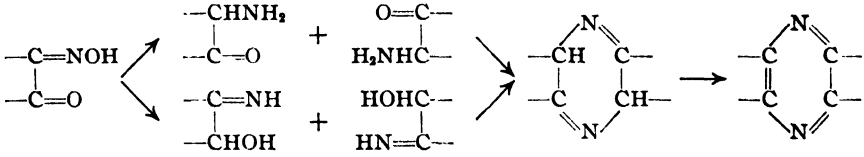
(1) Winans and Adkins, THIS JOURNAL, (a) 54, 306 (1932); (b) 55, 2051 (1933).

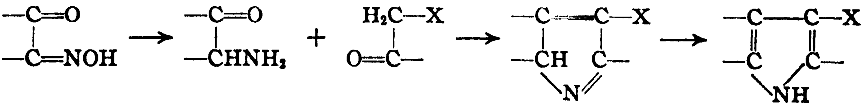
The present paper is concerned primarily with the application of these reactions in the synthesis and transformation of nitrogen ring compounds. A summary of the experimental results obtained in the synthesis of certain pyrrolidones, pyrazines and pyrroles is given in Table I, while in Table II is found a summary of the results in the hydrogenation and hydrogenolysis of certain α-amino nitriles, glyoxalones and pyrazolones.

Pyrazines.—The tendency toward the formation of pyrazines at the expense of open chain amines when α-oximino ketones or alcohols are subjected to hydrogenation over nickel has been noted previously in connection with the hydrogenation of benzil dioxime and benzoin oxime over nickel.[1b] Braun and Meyer[2] first observed this reaction in the reduction of oximes with sodium amalgam. The monoxime of benzil over nickel gave more tetraphenylpyrazine than of the open chain amino alcohol, while the oximino-acetoacetic ester, -acetophenone, and -hydrindone, gave only the corresponding pyrazines. The reaction (*cf.* IX) may be formulated as involving either the reaction of an amino with a carbonyl group or an imino with a hydroxyl group. In either case, the resulting dihydro pyrazine would be oxidized by air, according to Braun and Meyer, to the pyrazine



The second hypothesis must be assumed to explain the formation of a pyrazine from benzoin oxime, but since the yield of the pyrazine was much lower from benzoin oxime than from benzil oxime, reaction probably also proceeds according to the first hypothesis.

Pyrroles.—Knorr's[3] well-known and generally applicable synthesis of pyrroles involves the reduction with zinc and acetic acid of an α-oximino (isonitroso) ketone in the presence of a ketone having an active methylene group adjacent to the carbonyl. The type synthesis according to Knorr is as follows where X is acyl or carbalkoxy



The synthesis, in addition to the reduction, involves two types of reaction, one a Knoevenagel condensation of a ketone with an active methylene in the presence of an amine, and the other the reaction of an amine with a carbonyl.

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(2) Braun and Meyer, *Ber.*, **21**, 19 (1888).

(3) Knorr, *ibid.*, **17**, 1638 (1884); *Ann.*, **236**, 317 (1886); *cf.* Hollins, "Synthesis of Nitrogen Ring Compounds," D. Van Nostrand and Company, New York, 1924.

The application of catalytic hydrogenation at 100-200 atmospheres over nickel to the Knorr synthesis has been quite successful. The reactions proceeded to completion at temperatures of 50 to 90° within less than one hour. Success in the use of catalytic hydrogenation in this synthesis depends upon attaining conditions under which the oximino group is hydrogenated without the carbonyl group being affected. Eight variously substituted pyrroles as indicated in Table I have been prepared and isolated in yields of from 23 to 74%, the average being over 50%. The yields are, in the case of the five pyrroles previously reported, higher than those obtained by Knorr's original method. Knorr and Lange[4] obtained better yields (based upon the amino ketone) through the isolation and reaction of the latter with the β-diketone or β-keto ester.

TABLE I

SYNTHESIS OF PYRROLIDONES, PYRAZINES AND PYRROLES

Name and moles of hydrogen acceptors	Yield of products
Ethyl β-phenyl-β-cyanopyruvate (0.09)	26% 4-Phenyl-3-keto-pyrrolidone (m. p. 288–289°)
Ethyl β-phenyl-β-cyanopropionate (0.15)	89% 4-Phenylpyrrolidone (m. p. 76–77°)
Ethyl β-cyanopropionate (0.15)	38% Pyrrolidone (m. p. 23–26°)
Ethyl γ-oximinovalerate (0.10)	63% 5-Methylpyrrolidone (m. p. 33–35°)
Dimethylglyoxime (0.26)	18% 2,3-Diaminobutane (b. p. 145–155°)
	76% Tetramethylpyrazine hydrate (m. p. 76–77°)
Benzil monoxime (0.09)	42% Tetraphenylpyrazine (m. p. 242–243°)
	36% α,β-Diphenylethanolamine (m. p. 160–161°)
Oximinoacetoacetic ester (0.16)	43% 2,5-Dimethyl-3,6-dicarbethoxy-pyrazine (m. p. 87–88°)
Oximinoacetophenone (0.10)	54% 2,5-Diphenylpyrazine (m. p. 193–194°)
Oximinohydrindone (0.03)	78% 2,3,5,6-Di-indenopyrazine (m. p. 270–271°)
Oximinoacetoacetic ester (0.11); diacetylmethane (0.11)	63% 2,4-Dimethyl-3-acetyl-5-carbethoxypyrrole (m. p. 143–144°)
Oximinoacetoacetic ester (0.10); acetoacetic ester (0.10)	67% 2,4-Dimethyl-3,5-dicarbethoxypyrrole (m. p. 135–136°)
Oximinoacetophenone (0.10); acetoacetic ester (0.10)	35% 2-Methyl-3-carbethoxy-4-phenylpyrrole (m. p. 107°)
Oximinodiacetylmethane (0.10); acetoacetic ester (0.10)	74% 2,4-Dimethyl-5-acetyl-3-carbethoxypyrrole (m. p. 140–141°)
Oximinodibenzoylmethane (0.025); acetoacetic ester (0.025)	51% 2-Benzoyl-3-phenyl-4-carbethoxy-5-methylpyrrole (m. p. 156–157°)
Oximinohydrindone (0.03); acetoacetic ester (0.03)	44% 2-Methyl-3-carbethoxy-4,5-indenopyrrole (m. p. 199–200°)
	39% Ethyl β-amino-(1-hydroxy-N-2-hydrineno)-butyrate (m. p. 95–96°)
Oximinobenzoylacetylmethane (0.03); acetoacetic ester (0.03)	56% 2,4-Dimethyl-3-carbethoxy-5-benzoylpyrrole (m. p. 110–111°)
Oximinoacetoacetic ester (0.05); benzoyl acetonitrile (0.05)	23% 2-Phenyl-3-cyano-4-methyl-5-carbethoxypyrrole (m. p. 85–86°)

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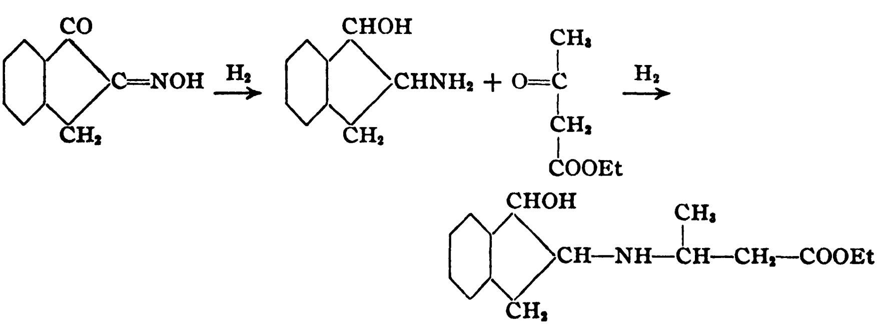
[4] Knorr and Lange, *Ber.*, **35**, 2998 (1902).

TABLE II

HYDROGENATION OF α-AMINO NITRILES, GLYOXALONES AND PYRAZOLONES

Name and moles of hydrogen acceptor	Yield of products
Methyleneaminoacetonitrile (0.59)	66% N-Methylethylenediamine 109–111°
	18% Di(β-N-methylaminoethyl)-amine 95–100° (25 mm.)
Diethylaminoacetonitrile (0.36)	37% N,N-Diethylethylenediamine 140–150°
	23% Di(β-diethylamino-ethyl)-amine130–135° (26 mm.)
Piperidinoacetonitrile (0.36)	50% β-Piperidino-ethylamine 80–85° (22 mm.)
	24% Di-(β-piperidinoethyl)-amine 160–170° (22mm.)
Piperidinoisobutyronitrile (0.24)	78% Piperidine 100–110° (740 mm.)
Piperidinocaprylonitrile (0.17)	79% Piperidine 100–110°
	22% n-Octylamine 85–87° (14 mm.)
Piperidinophenylacetonitrile (0.20)	82% Piperidine 100–110°
	50% β-Phenethylamine 75–80° (8 mm.)
	24% Di-β-phenethylamine 170–175° (8 mm.)
4,5-Diphenylglyoxalone (0.08)	82% 4,5 - Dicyclohexyl - dihydroglyoxalone, m. p. 237–239°
4,5-Dicyclohexylglyoxalone (0.04)	77% 4,5 - Dicyclohexyl - dihydroglyoxalone, m. p. 237–239°
4,5-Diethylglyoxalone (0.03)	76% 4,5-Diethyldihydroglyoxalone, m. p. 192–193°
1 - Phenyl - 3 - methylpyrazolone - 5 (0.11)	68% Butyranilide, m. p. 90–91°
1,3-Diphenylpyrazolone-5 (0.04)	95% β-Phenylpropionanilide, m. p. 89–90°
1 - Phenyl - 3 - methyl - 4 - benzalpyrazolone-5 (0.02)	80% α-Benzyl-β-aminobutyranilide (as hydrochloride)

The reaction of oximinohydrindone with acetoacetic ester gave a considerable yield of a product in addition to the pyrrole. Apparently to some extent the hydrogenation of the carbonyl group of oximinohydrindone preceded or accompanied the hydrogenation of the oximino group thus limiting the Knorr synthesis, for a yield of 39% of ethyl β-amino-(1 hydroxy N-2 hydrindeno)-butyrate was obtained, *i. e.*



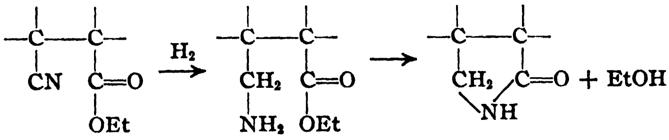
Knorr and Lange observed a similar reaction in attempting to prepare a pyrrole from oximinoacetone and methyl ethyl ketone.

It should be pointed out that isomeric pyrroles were formed from oximinoacetoacetic ester and diacetylmethane, and from oximinodiacetylmethane and acetoacetic ester. From this result it would seem reasonable to expect that such pairs of isomers could be prepared by switching the oximino group from one to the other of a pair of suitable compounds. However, such is not the case for from oximinoacetoacetic ester and dibenzoylmethane none of the expected pyrrole was obtained, but only a trace of 2,5-dimethyl-3,6-dicarbethoxypyrazine and large amounts of dibenzoylmethane. While oximinobenzoylacetylmethane plus acetoacetic ester was readily converted into a pyrrole, changing the oximino group from the diketone to the ester (oximinoacetoacetic ester and acetylbenzoylmethane) gave anomalous results. A compound of m. p. 128° was obtained in 89% yield (calculated as the pyrrole), but four rather than two molecular equivalents of hydrogen was absorbed in the process. The analysis for carbon showed 65.7 instead of 70.8 as calculated for the pyrrole, and the hydrogen was 7.13 instead of 6.27. The carbon content agreed with that for an amino alcohol in which one carbonyl group had been hydrogenated (thus making impossible the Knoevenagel condensation necessary for a Knorr pyrrole synthesis) but the hydrogen analysis was too low for this compound (7.85). The analysis for nitrogen gave values (5.03) between those for the pyrrole (5.16) and the amino alcohol (4.78). Similarly a product, m. p. 95–96°, analyzing low in carbon and high in hydrogen for a pyrrole, was obtained from the hydrogenation of a mixture of oximinopropiophenone and acetoacetic ester. Obviously, these data do not establish the nature of these two products but they do indicate that the course of the reaction is modified by the position of the oximino group.

The formation of a cyanopyrrole from oximinoacetoacetic ester and benzoyl acetonitrile is a new development of the pyrrole synthesis, and depends on the fact that over nickel a cyano group is less readily reduced than an oximino group. Under carefully controlled conditions the pyrrole synthesis was carried out without hydrogenation of the cyanide, giving rise to 2-phenyl-3-cyano-4-methyl-5-carbethoxypyrrole.

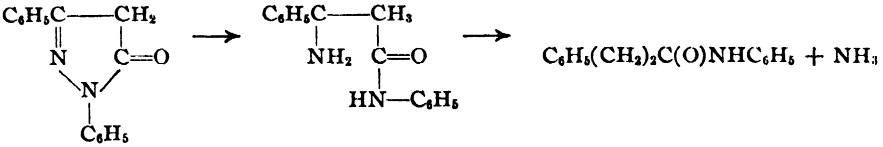
A crystalline product could not be isolated from the reaction mixture of oximinoacetoacetic ester and diethyl keto succinate.

Pyrrolidones.—Pyrrolidone itself and two derivatives, *i. e.*, 4-phenyl, and 4-phenyl-3-keto, were obtained by the hydrogenation at 50–90° of three β-cyano esters, the type reaction being as indicated



The amine produced by the hydrogenation of an oximino ester, γ-oximinovalerate, lost alcohol and 5-methylpyrrolidone was formed. The yields in all cases were greater than those previously reported for the preparation of these compounds.

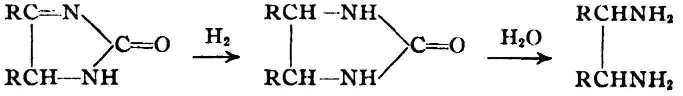
Pyrazolones.—The nitrogen to nitrogen bond in pyrazolones is apparently readily cleaved by hydrogen over nickel at 120–150° (*cf.* VII). Two pyrazolones which had no substituent in position 4 (*i. e.*, derived from β-keto esters having no α-substituent) underwent cleavage of the cycle with the subsequent elimination of ammonia to give a substituted amide. This reaction took place almost quantitatively with 1,3-diphenylpyrazolone-5 and to the extent of 68% with the 1-phenyl-3-methylpyrazolone.



$C_6H_5(CH_2)_2C(O)NHC_6H_5 + NH_3$

Pyrazolones having an ethyl, benzyl, benzal or β-phenylethyl radical in the 4 position apparently underwent a similar cleavage without the occurrence of the second step involving the elimination of ammonia. The hydrogen absorption was correct for this reaction and no ammonia was eliminated. The resulting β-amino anilides could not be purified satisfactorily. However, in the case of the 4-benzyl (or benzal) substituted pyrazolone an excellent yield (80%) of the hydrochloride of the α-benzyl-β-aminobutyranilide was isolated. The failure to obtain a similar product from the ethyl and β-phenylethyl substituted pyrazolones was apparently due to lack of material.

Glyoxalones.—Either 4,5-diphenyl- or dicyclohexyl-glyoxalone was hydrogenated at 200° in good yield (77–82%) to 4,5-dicyclohexyl dihydroglyoxalone. Similarly 4,5-diethylglyoxalone was converted into the corresponding dihydro compound. The relative ease of hydrogenation of the double bond in these two glyoxalones is to be contrasted with the complete resistance to hydrogenation of the similar double bond in the imidazole or glyoxaline series.[1b] The hydrogenation of the double bond in the glyoxalones renders available a method for the preparation of 1-2 diamines from the corresponding acyloins.



α-Aminonitriles.—The hydrogenation of six α-aminonitriles did not result in the development of a generally satisfactory method for the preparation of 1,2-diamines. Methyleneaminoacetonitrile was readily hydrogenated at 80–100° and a fair yield (66%) of N-methylethylenediamine was obtained. Diethyl aminoacetonitrile gave only a 37% yield of the desired amine, while four different α-piperidinonitriles underwent a rapid hydrogenolysis at the piperidino linkage and none of the desired β-piperidino-amine was obtained. This is a further example of the type of reaction listed as VIII above.

$$C_5H_{10}NCH(R)CN \longrightarrow C_5H_{10}NH + RCH_2CH_2NH_2$$

Experimental Part

The synthesis of the heterocyclic compounds listed in Table I was effected with approximately 4 g. of a Raney nickel catalyst.[5,6] The pyrrolidones were prepared in ether solution at 70–90°, absorption of hydrogen being complete in 0.75–1.0 hour. The pyrroles and pyrazines were formed in alcoholic solution at 70–90° in 0.75–1.0 hour. At this temperature hydrogenation of the oximino group was effected readily, and the resulting amino ketone condensed to give a pyrazine or pyrrole before the carbonyl group was reduced. The hydrogenations were, in general, carried out at the lowest temperature consistent with reasonable speed in an attempt to avoid side reactions. This hydrogenation temperature was found experimentally by observing the so-called "inflection point," the temperature above which the drop in pressure of hydrogen due to absorption was greater than the rise in pressure due to the heating of the bomb and contents. The "inflection temperature" is determined in part by the void in the bomb, which in this case was such that the drop in pressure per mole of hydrogen absorbed was about 2300 pounds per sq. inch.

In the synthesis of 4-phenyl-2,3-diketopyrrolidine, tetraphenylpyrazine, 2-methyl-3-carbethoxy-4,5-indenopyrrole, 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole, 2,4-dimethyl-5-acetyl-3-carbethoxypyrrole and 2,4-dimethyl-3,5-dicarbethoxypyrrole crystals of the reaction product had separated from the mixture in the bomb. These were redissolved in the reaction solvent, filtered from the used catalyst and recrystallized. In the other cases where no crystals had separated the reaction mixtures were filtered from the catalyst, allowed to evaporate in air for two to three days and then if necessary in a vacuum desiccator over sulfuric acid in order to effect crystallization. By this process a thick sirup was obtained in the preparation of 2-phenyl-3-cyano-4-methyl-5-carbethoxypyrrole. The sirup was extracted with hot methylcyclohexane from which were deposited long needles of the cyanopyrrole on evaporation of the solvent. This product was then easily recrystallized from methylcyclohexane.

Oximinohydrindone and acetoacetic ester gave a crystalline product from the reaction mixture which was difficultly soluble in 95% alcohol. This was the 2-methyl-3-carbethoxy-4,5-indenopyrrole referred to above. After removal of these crystals the addition of water to the mother liquor gave a precipitate of fine white crystals which after recrystallization from methylcyclohexane gave the correct analysis for ethyl β-amino-(1-hydroxy-N-2-hydrindeno)-butyrate.

Most of the heterocyclic compounds were recrystallized from 70% alcohol. Glacial acetic acid was used for tetraphenylpyrazine, and methylcyclohexane for 4-phenylpyrrolidone and 2-phenyl-3-cyano-4-methyl-5-carbethoxypyrrole. Pyrrolidone, 5-methylpyrrolidone and tetramethylpyrazine were isolated by distillation.

The hydrogenations of the α-aminonitriles listed in Table II were effected in ether or ethanol solution with approximately 8 g. of Raney nickel in half an hour at 80–100°. The products of the reaction were separated by distillation under reduced pressure through a small Widmer column.

The glyoxalones were hydrogenated at 200° with a kieselguhr supported nickel catalyst[7] in ethanol solution in three to five hours. The crystalline hydrogenation product had separated from the reaction mixture when the bomb was opened.

The pyrazolones were hydrogenated in ethanol at 150° with approximately 5 g. of

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(5) M. Raney, U. S. Patent 1,628,190 (May 19, 1927).

(6) Covert and Adkins, THIS JOURNAL, 54, 4116 (1932).

(7) Covert, Connor and Adkins, *ibid.*, 54, 1651 (1932).

Raney nickel in three hours. Evaporation of the reaction mixture in air deposited crystals of the anilides. The hydrochloride of the anilide of α-benzyl-β-aminobutyrate was formed in ether and had a m. p. of 155–156° after recrystallization from ethanol.

Anal. Calcd. $C_{17}H_{21}ON_2Cl$: Cl, 11.62. Found: Cl, 11.55.

The 4,5-dicyclohexylglyoxalone was prepared by refluxing 40 g. of duodecahydrobenzoin and 22 g. of urea in 150 ml. of glacial acetic acid for six hours. On cooling to room temperature crystals of the product separated. The reaction mixture was poured into 500 ml. of water, and the filtered product was washed with water to remove excess urea and acetic acid, and with ether to remove unchanged acyloin. After drying in air the product weighed 37 g. (82%), m. p. 287–289°.

The 4,5-diethylglyoxalone was prepared by refluxing 40 g. of propionin $C_2H_5C(O)CH(OH)C_2H_5$ and 35 g. of urea in 100 ml. of glacial acetic acid for six hours. The cooled solution from which some crystals had separated was poured into 400 ml. of water. The precipitated product was filtered, washed with water and recrystallized from 95% ethyl alcohol. After drying in air the product weighed 23 g. (44%) m. p. 293–294°.

The following compounds were prepared as previously described: ethyl β-phenyl-β-cyanopyruvate,[8] ethyl β-phenyl-β-cyanopropionate,[9] ethyl β-cyanopropionate,[10] oximinoacetoacetic ester,[11] oximino acetophenone,[12] oximinohydrindone,[13] oximinodiacetylmethane,[14] oximinodibenzoylmethane,[15] oximinobenzoyl acetone,[16] methyleneaminoacetonitrile,[17] diethylaminoacetonitrile,[18] piperidinoacetonitrile,[19] piperidinophenylacetonitrile,[19] 1-phenyl-3-methyl-pyrazolone-5,[20] 1,3-diphenylpyrazolone-5,[21] and 4,5-diphenylglyoxalone.[22]

The properties of the following list of compounds prepared in this investigation have been compared with those previously described by others: pyrrolidone,[23] 5-methylpyrrolidine,[24] 2,3-diaminobutane,[25] tetramethylpyrazine,[26] α,β-diphenylethanolamine,[27] tetraphenylpyrazine,[28] 2,5-dimethyl-3,6-dicarbethoxypyrazine,[29] 2,5-diphenylpyrazine,[30] 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole,[31] 2,4-dimethyl-3-ethyl-5-carbethoxypyrrole,[32] 2,4-dimethyl-3,5-dicarbethoxypyrrole,[33] 2-methyl-3-carbethoxy-4-phenylpyrrole,[34] 2,4-dimethyl-5-acetyl-3-carbethoxypyrrole,[35] 2,4-dimethyl-3-carbeth-

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(8) Erlenmeyer, *Ann.*, **271**, 173 (1892).

(9) Bredt and Kallen, *ibid.*, **293**, 344 (1896).

(10) Drusher, *Am. J. Sci.*, **187**, 544 (1914).

(11) Wahl and Beauveault, *Bull. soc. chim.*, [3] **33**, 554 (1905).

(12) Claisen and Manasse, *Ber.*, **20**, 2194 (1887).

(13) Gabriel and Stelzner, *ibid.*, **29**, 2604 (1896).

(14) Wolff, *Ann.*, **325**, 139 (1902).

(15) Neufville and Pechmann, *Ber.*, **23**, 3378 (1890).

(16) Wolff, *Ann.*, **325**, 136 (1902).

(17) "Organic Syntheses," Collective volume, 1932, p. 347.

(18) Klages and Margolinsky, *Ber.*, **36**, 4189 (1903).

(19) Knoevenagel, *ibid.*, **37**, 4023 (1904).

(20) Knorr, *Ann.*, **238**, 104 (1887).

(21) Knorr and Koltz, *Ber.*, **20**, 2846 (1887).

(22) "Organic Syntheses," Vol. XII, 1932, p. 34.

(23) Gabriel, *Ber.*, **22**, 3338 (1889).

(24) Tafel, *ibid.*, **22**, 1863 (1889).

(25) Morgan and Hickenbottom, *J. Soc. Chem. Ind.*, **43**, 307 (1924).

(26) Brandes and Stoehr, *J. prakt. Chem.*, [2] **53**, 501 (1896).

(27) Goldschmidt, *Ber.*, **20**, 493 (1887).

(28) Feist and Arnstein, *ibid.*, **28**, 3168 (1895).

(29) Wleügel, *ibid.*, **15**, 1050 (1882).

(30) Braun and Meyer, *ibid.*, **21**, 19 (1888).

(31) Zanetti and Levi, *Gazz. chim. ital.*, **54**, 547 (1894).

(32) Fischer and Wallach, *Ber.*, **58**, 2818 (1925).

(33) Knorr, *Ann.*, **236**, 317 (1886).

(34) Knorr and Lange, *Ber.*, **35**, 3002 (1902).

(35) Mognanini, *ibid.*, **21**, 2866 (1888).

oxy-5-benzoylpyrrole,[36] N-methylethylenediamine,[37] N,N-diethylethylenediamine,[38] β-piperidinoethylamine,[39] butyranilide,[40] β-phenylpropionanilide.[41]

Di-(β-methylaminoethyl)-amine (I), di(β-diethylaminoethyl)-amine (II), and di(β-piperidinoethyl)-amine (III) were isolated and characterized as picrates. There are given below in order for each of these derivatives the formula, m. p., neutral equivalent (calcd. and found), and analysis for picric acid (calcd. and found).

(I) $C_6H_{17}N_3 \cdot 3C_6H_3O_7N_3$; 172–173°; 43.6, 41; 83.9%, 83.6%
(II) $C_{12}H_{29}N_3 \cdot 3C_6H_3O_7N_3$; 165–166°; 71.6, 70; 76.1%, 76.2%
(III) $C_{14}H_{29}N_3 \cdot 3C_6H_3O_7N_3$; 210–211°; 79.6, 81; 74.0%, 73.6%

Picric acid was determined as nitron (diphenylenedoanilinohydrotriazole) picrate according to the method of Utz.[42]

In Table III are listed the names, melting points and analyses of compounds isolated and described herewith for the first time.

TABLE III

MELTING POINTS AND ANALYSES

Name	M. p., °C.	Formula	Calcd. C, %	Calcd. H, %	Found C, %	Found H, %
4-Phenyl-2,3-diketopyrrolidine	288–289	$C_{10}H_9O_2N$	68.5	5.18	68.6	5.25
2,3,5,6-Di-indenopyrazine	270–271	$C_{18}H_{12}N_2$	84.4	4.79	84.4	4.90
2-Benzoyl-3-phenyl-4-carbethoxy-5-methylpyrrole	156–157	$C_{21}H_{19}O_3N$	75.6	5.70	75.1	5.63
2-Methyl-3-carbethoxy-4,5-indenopyrrole	199–200	$C_{15}H_{15}O_2N$	74.7	6.22	74.8	6.28
Ethyl β-amino(1-hydroxy-N-2 hydrindeno)-butyrate	95–96	$C_{15}H_{21}O_3N$	68.5	7.98	68.7	7.86
2-Phenyl-3-cyano-4-methyl-5-carbethoxypyrrole	85–86	$C_{15}H_{15}O_2N_2$	70.9	5.51	71.2	5.62
4,5-Diethyldihydroglyoxalone	192–193	$C_7H_{14}ON_2$	59.1	9.93	58.9	9.80
4,5-Diethylglyoxalone	293–294	$C_7H_{12}ON_2$	59.9	8.67	59.7	8.71
4,5-Dicyclohexylglyoxalone	287–290	$C_{15}H_{24}ON_2$	72.6	9.68	72.5	9.78
4,5-Dicyclohexyldihydroglyoxalone	237–239	$C_{15}H_{26}ON_2$	72.1	10.45	71.9	10.44

Summary

Catalytic hydrogenation over nickel has been applied successfully to the Knorr synthesis of a number of pyrroles. Pyrrolidones have been prepared from cyano or oximino esters which upon hydrogenation yielded γ-amino esters. A number of pyrazines have been prepared from α-dioximes and α-oximino ketones, or alcohols. The double bond in glyoxalone in contrast to that in glyoxaline rings may be hydrogenated over nickel, thus making it possible to prepare 1,2-diamines from acyloins. The nitrogen to nitrogen bond in pyrazolones has been shown to be subject to hydrogenolysis. Deamination resulted in the case of certain pyrazolones but β-amino acid

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(36) Fischer, Schneller and Zerweck, *Ber.*, **55**, 2390 (1922).
(37) Johnson and Bailey, THIS JOURNAL, **38**, 2141 (1916).
(38) Ristenpart, *Ber.*, **29**, 2526 (1896).
(39) Gabriel, *ibid.*, **53**, 1991 (1920).
(40) Gerhardt, *Ann.*, **187**, 166 (1877).
(41) Hughes, *Ber.*, **25**, 747 (1892).
(42) Utz, *Z. anal. Chem.*, **47**, 140 (1908).

anilides from the pyrazolones substituted in the 4 position were stable, thus permitting the preparation of certain β-amino acids. The hydrogenation of α-aminonitriles to substituted 1,2-diamines has not been generally successful due in part to the ease of hydrogenolysis of compounds of this type.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

The Reaction between Aliphatic Orthoformates and Acetone

BY HOWARD W. POST

Ethyl orthoformate reacts with acetone in absolute ethyl alcohol solution to yield a compound known as a ketone acetal or ketal

$$CH_3COCH_3 + HC(OC_2H_5)_3 \longrightarrow HCOOC_2H_5 + (CH_3)_2C(OC_2H_5)_2 \qquad (1)$$

a drop or two of concentrated sulfuric acid or equally effective ammonium chloride, hydrochloric acid or pyridine hydrochloride acting as catalyst.[1]

It would seem at first glance that Equation 1 is not needed inasmuch as the ketone could be conceived as reacting with the alcohol, splitting off water which then would react with the ortho ester. Moreover, if it is the orthoformate which reacts, why is the alcohol necessary? To answer these questions and if possible to obtain information as to optimum conditions for the reaction, several runs were made using various solvents and catalysts, in most cases ethyl compounds.

The reagents, acetone, alcohol and orthoformate, were mixed in equimolecular amounts and allowed to stand at the temperature of the room (which was quite constant around 25°) for five to seven days. Where sulfuric acid was used as a catalyst the color of the solution darkened and the temperature rose as much as 10° during the first twenty-four hours. The products were isolated according to Claisen's method.[1]

Using the following amounts of reagents with various catalysts the following yields of ketals were obtained: 0.143 mole + 1 drop H_2SO_4, 13%; 0.286 mole + 1.3 g. NH_4Cl, 26%; 0.19 mole + 0.75 g. NH_4Cl, 30%; 0.68 mole + 1 drop HCl, 27%. Omission of the solvent or of the orthoformate gave zero yields. Using equimolecular amounts of isoamyl alcohol as a solvent also gave zero yields. Replacement of the ethyl alcohol by ethyl ether using 1 drop of sulfuric acid as catalyst gave an unchanged yield (13%).

A series of runs was then carried out to determine the applicability of this reaction to the preparation of higher homologs of diethyl ketal.

Equimolecular amounts of acetone, the alcohol and the corresponding orthoformate were used. In each case 0.15 g. of ammonium chloride was used as a catalyst for every hundredth mole of acetone. The amounts of acetone varied between one-tenth of a mole and four-tenths of a mole.

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[1] Claisen, *Ber.*, **29**, 1007 (1896); *ibid.*, **47**, 3171 (1914); Arbusow, *ibid.*, **40**, 3303 (1907); Tschitschibabin and Jelgasin, *ibid.*, **47**, 48 and 1851 (1914).

The orthoformates were prepared according to the methods in the literature.[2]

With propyl alcohol yields of 25–30% of dipropyl ketal were obtained. With butyl, isobutyl, amyl and isoamyl alcohols no ketals were obtained but considerable quantities of orthoformate were recovered (30–50%), the amount varying directly as the molecular weight in a qualitative sense.

Diethyl ketal and butyl alcohol were mixed in molecular proportions of 1:2 and allowed to stand for one week at room temperature and illumination. The products from this reaction were identified as dibutyl ketal and ethylbutyl ketal

$$(CH_3)_2C(OC_2H_5)_2 + C_4H_9OH \rightleftharpoons C_2H_5OH + (CH_3)_2C(OC_2H_5)OC_4H_9 \qquad (2)$$
$$(CH_3)_2C(OC_2H_5)OC_4H_9 + C_4H_9OH \rightleftharpoons C_2H_5OH + (CH_3)_2C(OC_4H_9)_2 \qquad (3)$$

No catalyst of any sort was added. Attempts to repeat this reaction with ketal and alcohol involving radicals close to each other in radical weight were unsuccessful because of inability to isolate the pure products. The physical constants of the products were too close together to make identification certain. In this run 10.0 g. of $(CH_3)_2C(OC_2H_5)_2$ was mixed with 11.2 g. of C_4H_9OH. A 16% yield of ethylbutyl ketal resulted, and a 10% yield of dibutyl ketal.

The properties of these ketals are shown in the table. Values for the refractive indices are taken from the literature.[3]

KETALS

Alkyls	B. p., °C. (mm.)	n^{22}	d_4^{22}	N, % Calcd.	N, % Found
Diethyl	112 (736.4)	1.3867	0.820	37.81	37.84
Ethyl, butyl	74–77 (30); 122 (745.9)	1.4049	.867	47.05	45.25
Dipropyl	77 (30); 125 (745.9)	1.4022	.8319	47.05	46.79
Dibutyl	93 (30); 130 (745.9)	1.4084	.824	56.28	56.18

"n" and "d" of diethyl ketal were taken at 21 and 21/4°, respectively.

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[2] "Organic Syntheses," **5**, 55 (1925); Sah and Ma, THIS JOURNAL, **54**, 2964 (1932).

[3] Landolt and Börnstein, "Physikalisch-chemische Tabellen," Vol. II, 985 (5th ed.).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

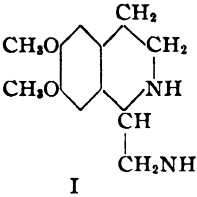
Isoquinoline Derivatives. II. Synthesis of 1-Aminomethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline

BY H. J. HARWOOD[1] AND T. B. JOHNSON

In continuing a study of the effect of various groups on the pharmacological action of isoquinoline derivatives the preparation of a 1-aminomethylisoquinoline appeared to be of particular interest because of the combined isoquinoline and β-phenylethylamine groupings.

Child and Pyman[2] attempted to prepare such an aminomethylisoquinoline by the action of ammonia and of potassium phthalimide on 1-chloromethyl-6,7-dimethoxy-3,4-dihydroisoquinoline but without success. These authors also dehydrated α-benzamido-N-(3,4-dimethoxyphenylethyl)-acetamide in the hope of obtaining 1-benzamidomethyl-6,7-dimethoxy-3,4-dihydroisoquinoline which could then be converted into the amino derivative. The desired compound was not obtained, however; a double ring-closure took place with the formation of 5,6-dihydro-8,9-dimethoxy-3-phenyl-imidaz-(4,3-α)-isoquinoline.

1-Aminomethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (I) has been prepared in this Laboratory. N-(3,4-Dimethoxyphenylethyl)-α-phthalimidoacetamide was dehydrated to give 1-phthalimidomethyl-6,7-dimethoxy-3,4-dihydroisoquinoline. The latter was reduced catalytically to the 1,2,3,4-tetrahydro derivative, which was then hydrolyzed to yield the desired aminoisoquinoline I.



I

The attempted ring closure of N-(β-phenylethyl)-α-phthalimidoacetamide to form 1-aminomethyl-3,4-dihydroisoquinoline yielded only an extremely small amount of product which was not investigated further.

A second and much simpler method of preparing I seemed possible through the ring closure of N-(3,4-dimethoxyphenylethyl)-α-triazoacetamide followed by catalytic reduction. Attempts to carry out this reaction were without success. The ring closure of α-amino-N-(3,4-dimethoxyphenylethyl)-acetamide hydrochloride was also unsuccessful.

TABLE I

Compound	Yield, %		Analyses, % Calcd.	Found	
Phthalylglycine[a] (m. p. 191–192.5°)	86		...	...	...
Phthalylglycyl chloride[b]	77		...	...	...
N-(β-Phenylethyl)-α-phthalimidoacetamide[c]	91	N,	9.09	8.63	8.76
N-(3,4-Dimethoxyphenylethyl)-α-phthalimidoacetamide[d]	72	N,	7.61	7.20	7.22

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[1] E. R. Squibb and Sons Research Fellow in Organic Chemistry.

[2] Child and Pyman, *J. Chem. Soc.*, 36 (1931).

TABLE I (*Concluded*)

Compound	Yield, %	Analysis, % Calcd.	Found	
1-Phthalimidomethyl-6,7-dimethoxy-3,4-dihydroisoquinoline[e]	87	C, 68.53	68.62	...
		H, 5.18	5.18	...
		N, 8.00	7.93	...
1-Phthalimidomethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline hydrochloride[f]	..	C, 61.74	61.24	...
		H, 5.45	5.61	...
		Cl, 9.12	8.74	...
1-Aminomethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline sulfate[g]	..	C, 44.97	45.36	...
		H, 6.30	6.51	...
		S, 10.01	10.12	...
Triazoacetyl chloride[h]	78	...	...	...
N-(3,4-Dimethoxyphenylethyl)-α-triazoacetamide[i]	80	C, 54.52	54.87	...
		H, 6.11	6.14	
α-Amino-N-(3,4-dimethoxyphenylethyl)-acetamide hydrochloride[j]	87	Cl, 12.91	12.70	12.60

[a] From glycine and phthalic anhydride according to the method of Drechsel.[3]

[b] From phthalylglycine and thionyl chloride; b. p. 172–174° (5 mm.). Gabriel[4] gives 84–85° as the melting point.

[c] From phthalylglycyl chloride, β-phenylethylamine and 10% sodium hydroxide solution. Crystallized from alcohol. An attempt to bring about ring closure in this amide using phosphorus oxychloride in boiling toluene was unsuccessful. Using phosphorus pentoxide in boiling xylene a very small amount of basic product was obtained which was not investigated further.

[d] From phthalylglycyl chloride, homoveratrylamine[5] and 6% sodium carbonate solution. Crystallized from alcohol.

[e] By treatment of above amide with phosphorus oxychloride in boiling toluene for one and one-half hours. Toluene diluted with petroleum ether and precipitate dissolved in hot water and product precipitated with ammonium hydroxide. Crystallized from alcohol. If the above aqueous solution is allowed to cool without the addition of alkali, yellow crystals of a "phosphate" of undetermined constitution separate; sulfate obtained by diluting an alcoholic sulfuric acid solution with ether. Crystallized from absolute alcohol, m. p. 229–231°.

Anal. Calcd. for $C_{20}H_{18}N_2O_4 \cdot H_2SO_4 \cdot H_2O$: H_2O, 3.86. Found: loss at 60° and 3 mm., 3.93, 3.75. Calcd. for $C_{20}H_{18}N_2O_4 \cdot H_2SO_4$: S, 7.14. Found: S, 6.87 and 6.75.

[f] Prepared by the catalytic reduction of the dihydroisoquinoline. The reduction was carried out either on a dilute hydrochloric acid solution of the free base or on an aqueous solution of the "phosphate" at 3 atmospheres pressure using Adams platinum oxide catalyst. The isoquinoline hydrochloride was obtained by evaporation of the solution and was recrystallized from alcohol. Thirteen grams of dihydroisoquinoline "phosphate" yielded 10 g. of tetrahydroisoquinoline "phosphate," m. p. 244–245° (effervescence).

[g] Ten grams of the above phthalimido-tetrahydroisoquinoline "phosphate" was suspended in 30 cc. of alcohol and treated with 3 cc. of hydrazine hydrate. The mixture was warmed until all had dissolved, cooled and the gelatinous mass treated with an excess of dilute hydrochloric acid and warmed. The phthalic acid which separated was filtered and the filtrate evaporated to dryness. An attempt was made to convert this crude isoquinoline salt into the sulfate by treating an aqueous solution with about 50% sul-

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(3) Drechsel, *J. prakt. Chem.*, [2] **27**, 418 (1883).

(4) Gabriel, *Ber.*, **40**, 2647 (1907).

(5) Prepared as previously described, Harwood and Johnson, THIS JOURNAL, **55**, 2555 (1933).

furic acid. The sulfate failed to precipitate. The solution was neutralized with sodium hydroxide, filtered from sodium sulfate and evaporated to a volume of about 100 cc. Upon making strongly alkaline with sodium hydroxide the aminoisoquinoline separated as a viscous oil. The aqueous layer was removed by means of a separatory funnel, the oil dissolved in a small volume of water and made just acid by the addition of 50% sulfuric acid. Upon diluting with alcohol a mass of white crystals formed. After recrystallization from dilute alcohol the 1-aminomethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline sulfate melted with effervescence at about 274–275°. The melting point varied considerably with the rate of heating. A yield of 3.4 g. of pure product was obtained.

Anal. Calcd. for $C_{12}H_{18}N_2O_2 \cdot H_2SO_4 \cdot 2H_2O$: H_2O, 10.12. Found: loss at 60° and 3 mm., 10.27, 10.38.

[h] Prepared according to the method of Bertho and Maier.[6]

[i] Six grams of homoveratrylamine was dissolved in 10 cc. of water, cooled in an ice-bath and with shaking treated alternately with small portions of *N* sodium hydroxide solution and triazoacetyl chloride. A total of 4.4 g. of acid chloride and 33 cc. of sodium hydroxide solution was used. The product separated as an oil which finally solidified and was crystallized from benzene. Attempts to bring about ring closure in this compound using phosphorus oxychloride in boiling toluene or benzene, phosphorus pentoxide in boiling xylene and phosphorus pentachloride in chloroform at room temperature were without success.

[j] Four grams of the above amide was dissolved in 50 cc. of alcohol and hydrogenated at 3 atmospheres pressure using Adams platinum oxide catalyst. After two hours the solution was filtered, treated with 1.25 cc. of concentrated hydrochloric acid and evaporated to dryness under reduced pressure. The residue was extracted with 30 cc. of hot absolute alcohol in several portions and the hot solution diluted with an equal volume of dry ether. A white crystalline precipitate separated which weighed 3.6 g. and was recrystallized from alcohol–ether. An attempt was made to bring about ring closure in this amide using phosphorus pentachloride in chloroform at room temperature. No definite product could be isolated.

Summary

1. Starting with phthalylglycyl chloride and homoveratrylamine, N-(3,4-dimethoxyphenylethyl)-α-phthalimidoacetamide has been prepared in good yield.

2. By treatment with phosphorus oxychloride this amide undergoes a molecular condensation giving 1-phthalimidomethyl-6,7-dimethoxy-3,4-dihydroisoquinoline. The latter when reduced catalytically is converted smoothly into the corresponding 1,2,3,4-tetrahydroisoquinoline.

3. This 1,2,3,4-tetrahydroisoquinoline interacts smoothly with hydrazine hydrate to give 1-aminomethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline.

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(6) Bertho and Maier, *Ann.*, **498**, 50 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHEKIANG, CHINA]

Researches on Pyrimidines. The Molecular Rearrangement of 2-Ethylmercapto-5-phenyl-6-thiocyanopyrimidine[1,2]

BY YUOH-FONG CHI AND YU-LIN TIEN

A further study of the behavior of potassium thiocyanate toward imino chlorides of the pyrimidine type has led to interesting results which are now reported in this paper. Following the technique of Wheeler, Johnson[3] and co-workers, the authors have investigated the action of 2-ethylmercapto-5-phenyl-6-chloropyrimidine[3] (II) on thiocyanates and find that they interact smoothly to form a normal thiocyanate (III). The structure of this rhodanide is established by the fact that it undergoes a normal change when allowed to interact with a thiol acid[3b,d,4] giving 2-ethylmercapto-5-phenyl-6-thiopyrimidine, V. This new thiocyanpyrimidine (III) exhibits a chemical behavior similar to that of 2-ethylmercapto-5-carbethoxy-6-thiocyanpyrimidine[3d] and 2-ethylmercapto-4-methyl-6-thiocyanpyrimidine.[3e] It can be distilled under a pressure of 2 mm. at 215° without decomposition and without molecular conversion into its isothiocyanate modification, IV. The stability of the rhodanide (III) is greatly influenced by the presence of certain reagents, and a molecular rearrangement to the corresponding isothiocyanate (IV) can be accomplished easily at a temperature very much below that of the boiling point of the pyrimidine thiocyanate. The conditions under which this change is brought about are described in the experimental part of this paper.

$NHC(SC_2H_5){=}NHC{=}C(C_6H_5)CO$ I

$NC(SC_2H_5){=}NCH{=}C(C_6H_5)CCl$ II

$NC(SC_2H_5){=}NCH{=}C(C_6H_5)CSCN$ III

$NC(SC_2H_5){=}NCH{=}C(C_6H_5)CNCS$ IV

$NHC(SC_2H_5){=}NCH{=}C(C_6H_5)CS$ V

Experimental Part

2-Ethylmercapto-5-phenyluracil (I).—To an aqueous solution of the sodium salt of ethylformylacetate, prepared from 71 g. of ethyl phenylacetate and 38 g. of ethyl formate in the presence of 10 g. of metallic sodium in ether solution, 50 g. of pseudo-

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[1] This paper is a report of one phase of a research program dealing with the chemistry of certain pyrimidine thiocyanates, which was started originally in the Sterling Chemistry Laboratory of Yale University under the direction of Professor Treat B. Johnson.

[2] This research has been accomplished and arranged for publication through the support of a grant from the Rockefeller Foundation. The authors desire to express here their appreciation and thanks for this liberal assistance.

[3] (a) Wheeler and Bristol, *Am. Chem. J.*, **33**, 448 (1905); (b) Johnson and McCollum, *ibid.*, **36**, 136 (1906); (c) Johnson and Storey, *ibid.*, **40**, 131 (1908); (d) Johnson and Chi, THIS JOURNAL, **52**, 1580 (1930); (e) Chi and Chen, *ibid.*, **54**, 2056 (1932);

[4] Wheeler and Merriam, *ibid.*, **23**, 283 (1901).

ethylthiourea hydrogen bromide was dissolved. A cold solution of 10.6 g. of sodium hydroxide dissolved in 20 cc. of water, was then added very slowly. The mixture was left overnight in an ice box. On acidifying this alkaline solution with acetic acid, the oxypyrimidine separated. After purification by crystallization from 95% alcohol, it melted at 153–154° to a clear oil. The yield of the pure oxypyrimidine was 33 g. It is soluble in hot water and alcohol.

Anal. Calcd. for $C_{12}H_{12}ON_2S$: N, 12.07. Found: N, 11.91, 11.86.

2-Ethylmercapto-5-phenyl-6-chloropyrimidine, II.—Twenty grams of 2-ethylmercapto-5-phenyluracil was dissolved in 60 cc. of cold phosphorus oxychloride and the solution heated in an oil-bath at 130–140° for nine hours. After the removal of the excess of phosphorus oxychloride under diminished pressure, there was left a sirup, which would not solidify on cooling. It was treated with cracked ice in order to decompose double phosphorus compounds, the temperature never being allowed to rise above 0°. It was then extracted with ether and the ethereal solution dried with anhydrous calcium chloride. After the ether was distilled off, it left a yellow oil which solidified on cooling. It distilled as follows: 72 mm. at 175°, 10 mm. at 218°, and 20 mm. at 231–232°. The product solidified in the receiver, and melted at 38–39°. The yield was 15 g. or 70%. It is insoluble in water but very soluble in alcohol, benzene, and petroleum ether. On account of its great solubility in most organic solvents, it cannot be purified by crystallization.

Anal. Calcd. for $C_{12}H_{11}N_2SCl$: N, 11.18. Found: N, 11.16, 10.96.

2-Ethylmercapto-5-phenyl-6-thiocyanpyrimidine, III.[5]—This compound can be obtained by the action of potassium thiocyanate on the above chloride in boiling alcohol or benzene solutions. Fifteen grams of the chloropyrimidine, boiling at 175° at 2 mm. pressure, and 10 g. of potassium thiocyanate were dissolved in 40 cc. of absolute alcohol and the solution refluxed on a water-bath for one-half hour, when the reaction was complete. The solution was filtered while hot and chilled, when the thiocyanate separated immediately in the form of colorless needles. The yield was 16 g. or 97%. After purification by crystallization from benzene and ligroin (1:1), it separated as colorless flat needles and melted at 90° to a colorless oil. It distilled at 215° under a pressure of 2 mm. It can also be purified by crystallization from alcohol. The thiocyanate is insoluble in alkali but soluble in benzene, toluene and xylene, very soluble in hot alcohol and insoluble in petroleum ether.

Anal. Calcd. for $C_{13}H_{11}N_3S_2$: N, 15.38. Found: N, 15.30, 15.32.

Proof of Structure of the Thiocyanate.—That the compound described above (melting at 90°) is to be represented by a normal rhodanide or thiocyanate structure is established by the following experimental facts: (1) it does not undergo any change leading to the formation of a thiourea when exposed to the action of concentrated aqueous ammonia, (2) it can be crystallized from hot alcohol without conversion to a thiourethan and (3) the compound reacts with thioacetic acid to form the thiopyrimidine described below.

2-Ethylmercapto-5-phenyl-6-thiopyrimidine, V.—Two grams of 2-ethylmercapto-5-phenyl-6-thiocyanopyrimidine was dissolved in 10 cc. of thioacetic acid and the solution warmed on a water-bath for six to eight hours. After cooling, the thiopyrimidine separated in the form of yellow needles. It was purified by crystallization from absolute alcohol, and separated on cooling in the form of yellow plates melting at 171° to a clear oil.

Anal. Calcd. for $C_{12}H_{12}N_2S_2$: N, 11.29. Found: N, 11.30, 11.28.

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(5) The pyrimidine chloride and thiocyanate experiments were first performed by Miss Tse Yuh Ho and were described in her thesis submitted to the Faculty of the College of Arts and Sciences of the University of Chekiang as a partial fulfilment of the requirements for the B.S. degree from that institution in June, 1932.

This compound was identified as 2-ethylmercapto-5-phenyl-6-thiopyrimidine as follows. When mixed with the thiopyrimidine prepared by the action of sodium hydrosulfide upon the corresponding chloropyrimidine, the melting point was not altered.

The procedure used for preparing the thiopyrimidine by interaction of the chloropyrimidine and sodium hydrosulfide was as follows. Four grams of the corresponding chloropyrimidine and 1 g. of freshly prepared sodium hydrosulfide were dissolved in 15 cc. of absolute alcohol, and the solution heated to boiling for two hours. It was slightly acidified with one drop of glacial acetic acid. The solution was filtered to separate the insoluble sodium chloride, while hot, and when cooled the thiopyrimidine separated in the form of yellow needles. It was purified by crystallization from absolute alcohol and melted at 171°. The yield was 52%.

Anal. Calcd. for $C_{12}H_{12}N_2S_2$: N, 11.29. Found: N, 11.32.

The Molecular Rearrangement of 2-Ethylmercapto-5-phenyl-6-thiocyanopyrimidine into its Isomeric Form, IV

2-Ethylmercapto-5-phenyl-6-isothiocyanopyrimidine, IV.—Four grams of the thiocyanate was refluxed in 10 cc. of xylene for thirty hours, giving a red colored solution. After distilling off xylene, the isothiocyanate residue was extracted with petroleum ether and the solution concentrated and finally chilled, when the isothiocyanate separated in the form of colorless needles. The yield was about 70%. The compound was purified by crystallization from petroleum ether, and melted at 84–85° to an oil. On standing, the isothiocyanate becomes colored.

Anal. Calcd. for $C_{13}H_{11}N_3S_2$: N, 15.38. Found: N, 15.01.

Proof of Structure of the Isothiocyanate, IV

2-Ethylmercapto-5-phenyl-6-thioureapyrimidine $C_{13}H_{14}N_4S_2$.—The thiocyanate was rearranged into the isothiocyanate form as described above and a petroleum ether solution of the latter combined with an excess of concentrated aqueous ammonia. The corresponding thiourea was formed immediately and 2.4 g. was obtained from 4 g. of the thiocyanate. It was purified by crystallization from ethyl acetate and it separated in colorless needles melting at 204° to a clear oil.

Anal. Calcd. for $C_{13}H_{14}N_4S_2$: N, 19.31. Found: N, 19.22, 19.02.

2-Ethylmercapto-5-phenyl-thioureapyrimidine, $C_{19}H_{18}N_4S_2$.—Four grams of the rearranged thiocyanate gave 3.2 g. of this compound by treatment with aniline at ordinary temperature. This was purified by crystallization from a benzene–ligroin mixture and separated in yellow needles melting at 149°.

Anal. Calcd. for $C_{19}H_{18}N_4S_2$: N, 15.30. Found: N, 15.14, 15.02.

2-Ethylmercapto-5-phenyl-6-thionethylurethan-pyrimidine $C_{15}H_{17}ON_3S_2$.—Four grams of the thiocyanate was rearranged to the isothiocyanate modification and then dissolved in 10 cc. of absolute alcohol. The solution was heated for a few minutes, and on cooling the urethan separated in the form of colorless needles. The yield was 2.5 g. or about 53% of the theoretical. After crystallization from alcohol it melted at 85–85.5°.

Anal. Calcd. for $C_{15}H_{17}ON_3S_2$: N, 13.16. Found: N, 13.17, 13.18.

2-Ethylmercapto-5-phenyl-6-thionmethylurethan Pyrimidine, $C_{14}H_{15}ON_3S_2$.—This was formed by warming the crude isothiocyanate with 10 cc. of methyl alcohol. It crystallized from methyl alcohol in the form of colorless needles melting at 79–80° to a clear oil.

Anal. Calcd. for $C_{14}H_{15}ON_3S_2$: N, 13.77. Found: N, 13.87, 13.62.

Experimental Conditions Influencing the Rearrangement of the Pyrimidine Thiocyanate.—A. While the thiocyanate can be distilled under diminished pressure without change into the isothiocyanate modification, it can be rearranged at a temperature much lower than its boiling point. Heating of the thiocyanate at 120° for three hours gave an oil, in which there was not any detectable amount of the isothiocyanate modification. Digestion of the pyrimidine thiocyanate in benzene did not produce a rearrangement. Heating in xylene solution for ten hours produced no change; but the change was brought about by refluxing in xylene solution for thirty hours.

B. At the boiling point of ethyl alcohol the pyrimidine thiocyanate undergoes no change and can be crystallized repeatedly from this solvent without structure alteration. On heating in alcohol at 100° for six hours the thiocyanate also undergoes no change. On the other hand, when heated in alcohol solution at 140° (75° below its boiling point) the thiocyanate is transformed into the isothiocyanate and the latter combines with alcohol, giving the corresponding thionurethan. Two grams of the thiocyanate dissolved in 10 cc. of absolute alcohol was heated at 140° for two hours. After the tube was opened, the solution was left in an ice box for two weeks. The thionethylurethan separated extremely slowly. The yield was one gram. This crystallized from alcohol and melted sharply at 85°. Mixed with the thionethylurethan described above, the melting point was not altered.

Summary

1. 2-Ethylmercapto-5-phenyluracil has been prepared by condensing the sodium salt of ethylformylphenylacetate with pseudoethylthiourea hydrogen bromide in the presence of alkali.

2. This uracil derivative interacts with phosphorus oxychloride to form 2-ethylmercapto-5-phenyl-6-chloropyrimidine.

3. 2-Ethylmercapto-5-phenyl-6-thiocyanpyrimidine is formed by interaction of potassium thiocyanate with 2-ethylmercapto-5-phenyl-6-chloropyrimidine in boiling ethyl alcohol or benzene solutions.

4. This pyrimidine thiocyanate distils at 215° at 2 mm. pressure and is rearranged to its isomeric form, the isothiocyanate, (1) by heating with alcohol at 140° and (2) by digestion in boiling xylene. Both the thiocyanate and the isothiocyanate can be obtained as crystalline compounds.

5. The structure of the thiocyanate is established by interaction of the compound with thioacetic acid. This gives 2-ethylmercapto-5-phenyl-6-thiopyrimidine, which can also be synthesized normally by the action of sodium hydrosulfide on the corresponding chloropyrimidine.

6. The thiocyanate does not interact with alcohols, ammonia or aniline. The isothiocyanate reacts with these same reagents to form the corresponding thionurethans and thioureas, respectively.

HANGCHOW, CHEKIANG, CHINA

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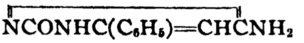
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHEKIANG, CHINA]

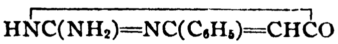
Researches on Pyrimidines. Synthesis of 5-Phenylcytosine

BY YUOH-FONG CHI AND YU-LIN TIEN

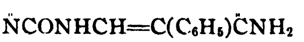
If we limit ourselves to carbon substituted pyrimidines there are only four phenyl derivatives of cytosine and isocytosine to be considered, namely, the phenyl constructions represented by formulas I, II, III and IV, respectively.


$NCONHC(C_6H_5){=}CHCNH_2$

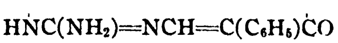
I


$HNC(NH_2){=}NC(C_6H_5){=}CHCO$

II


$NCONHCH{=}C(C_6H_5)CNH_2$

III


$HNC(NH_2){=}NCH{=}C(C_6H_5)CO$

IV

Jaeger[1] and Warmington[2] independently prepared 4-phenylisocytosine II by the interaction of guanidine carbonate with ethyl benzoylacetate, and their observation was confirmed later by the work of Johnson and Hill.[3] The latter investigators also made the interesting observation that this pyrimidine II occurs in four isomeric crystalline modifications. Later Johnson and Hemingway[4] synthesized the 4-phenylcytosine I, but, so far as the authors are aware, 5-phenylcytosine III and 5-phenylisocytosine have not been prepared. The object of this short paper is to report our method of synthesizing the new phenylcytosine derivative represented by formula III.

Our method of procedure was to start with 2-ethylmercapto-5-phenyluracil and prepare first 2-ethylmercapto-5-phenyl-6-chloropyrimidine according to the technique of Chi and Tien.[5] This chloropyrimidine reacted smoothly with ammonia in alcohol solution at 150°, forming 2-ethylmercapto-5-phenyl-6-aminopyrimidine V, $NC(SC_2H_5){=}NCH{=}C(C_6H_5)CNH_2$. When digested with hydrobromic acid this aminopyrimidine was destroyed with evolution of ethylmercaptan, yielding the hydrobromide of the desired 5-phenylcytosine III in good yield. The free pyrimidine base was easily obtained by treatment of its hydrobromide with ammonia.

Experimental Part

2-Ethylmercapto-5-phenyl-6-aminopyrimidine, V.—This pyrimidine is formed by heating 2-ethylmercapto-5-phenyl-6-chloropyrimidine[6] with strong alcoholic ammonia at 150°. Usually about four hours of heating are necessary to bring about a complete reaction. The cooled reaction mixture is filtered to separate undissolved ammonium chloride and the alcohol solution finally evaporated to dryness. The residue left behind

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(1) Jaeger, *Ann.*, **262**, 373 (1890).

(2) Warmington, *J. prakt. Chem.*, [2] **47**, 214 (1893).

(3) Johnson and Hill, THIS JOURNAL, **36**, 1202 (1914).

(4) Johnson and Hemingway, *ibid.*, **37**, 378 (1915).

(5) Chi and Tien, *ibid.*, **55**, 4181 (1933).

was then extracted with boiling benzene, and the filtered benzene solution diluted with petroleum ether. On cooling the desired aminopyrimidine separated in the form of colorless rhombic crystals. It was purified by recrystallization from a benzene-petroleum ether mixture and it melted at 87–88° to a clear oil. The yield from 16 g. of the chloropyrimidine was 8.5 g.

Anal. Calcd. for $C_{12}H_{13}N_3S$: N, 18.18. Found: N, 18.38, 18.39.

5-Phenylcytosine, III.—This pyrimidine was obtained in the form of its hydrobromic acid salt by hydrolysis of 2-ethylmercapto-5-phenyl-6-aminopyrimidine with hydrobromic acid. Five grams of the mercaptopyrimidine was dissolved in 20 cc. of hydrobromic acid (48%) and the mixture refluxed on a sand-bath for fifteen hours, when the evolution of ethylmercaptan had ceased. The hydrobromide separated on cooling. After evaporating the excess of acid the salt was then purified by crystallization from water. It separated in the form of colorless long needles which sintered at 270° and melted at 280–281° with decomposition. The yield of the hydrobromide was 3.5 g. It was dried in a vacuum desiccator and analyzed.

Anal. Calcd. for $C_{10}H_{10}ON_3Br$: N, 15.68. Found: N, 15.52, 15.32.

In order to obtain the free pyrimidine base (5-phenylcytosine), this hydrobromide was dissolved in water and the hydrobromic acid neutralized by adding aqueous ammonia solution. The pyrimidine separated at once in a crystalline condition. The base is insoluble in cold ammonia but soluble in sodium hydroxide solution. The pyrimidine is soluble in boiling water and 95% alcohol. It crystallizes from water in the form of colorless needles and from alcohol in the form of colorless rhombic prisms. The yield from 1 g. of the hydrobromide is 0.6 g. The pyrimidine does not melt or decompose below 310°. It was dried over concentrated sulfuric acid in a vacuum desiccator and analyzed.

Anal. Calcd. for $C_{10}H_9ON_3$: N, 22.46. Found: N, 22.52, 22.57.

Hydrochloride $C_{10}H_9ON_3 \cdot HCl$.—This salt is easily obtained by dissolving the 5-phenylcytosine in dilute hydrochloric acid and then allowing the solution to crystallize. It separated in the form of colorless needles which sintered at 270° and melted at 277–278°. For analysis, the salt was recrystallized from water and dried at 120°.

Anal. Calcd. for $C_{10}H_{10}ON_3Cl$: N, 18.80. Found: N, 18.85.

Summary

1. The action of alcoholic ammonia upon 2-ethylmercapto-5-phenyl-6-chloropyrimidine gives the corresponding aminopyrimidine, 2-ethylmercapto-5-phenyl-6-aminopyrimidine.

2. This mercaptopyrimidine is hydrolyzed by digestion with hydrobromic acid, giving 5-phenylcytosine hydrobromide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND OF LENOIR RHYNE COLLEGE]

A Chemical Examination of the Volatile Oil of Sarothra Gentianoides L. and the Detection Therein of Normal Nonane[1]

BY MARSTON TAYLOR BOGERT AND SIMON J. MARION

The solid members of the paraffin series are quite widely distributed in the plant kingdom, where they often appear as waxy coatings or excretions on various parts of the plant. Naturally, because of their relatively high boiling points, they are not so often found in the volatile oils obtained from these plants by distillation, although occasionally they are present in sufficient amount to cause the oil to congeal at temperatures but little below the normal, as is the case with the atar of rose, for example.

Of the liquid paraffins, on the other hand, the only one definitely identified as a plant constituent is the *n*-heptane which has been reported in the *Pinus sabiniana* and *Pinus jeffreyi* of California and in the "petroleum nuts" of the *Pittosporum resiniferum*, from the Philippine Islands. Brooks, in his well-known volume on "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Inc., New York, 1922, remarks (p. 89) that "Normal heptane enjoys the distinction of being the only saturated hydrocarbon, other than the solid paraffins, formed by phytochemical processes."

It has been reported[2] that the crude wood turpentine produced by the destructive distillation of the longleaf pine contains pentane, but this report lacks confirmation.

Some six years ago, the late Dr. Emerson R. Miller[3] described a preliminary investigation of the volatile oil of *Hypericum perforatum*, in the course of which he collected a low-boiling fraction, whose properties were such as to suggest the presence therein of an aliphatic hydrocarbon not hitherto discovered in any essential oil. Based upon our own results, as recorded beyond, with a closely related species, it seems to us quite probable that Dr. Miller was right in believing that this low-boiling fraction from *H. perforatum* consisted largely of a nonane,[4] although of course this still remains to be proved.

The family of the *Hypericaceae*, containing some ten genera and over 300 species, includes the well-known St. John's Wort, or *Hypericum*, genus, of which only *H. perforatum*, as noted above, seems to have been studied to any extent, either pharmacologically[5] or chemically. From the days of Dioscorides, who lived about the first century A. D., the St. John's Worts

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(1) Presented before the Division of Medicinal Chemistry, at the Meeting of the American Chemical Society, Washington, D. C., March 28, 1933.

(2) Parry, "The Chemistry of Essential Oils," Scott, Greenwood & Son, London, 1921, I, p. 17

(3) Miller, *J. Am. Pharm. Assoc.*, **16**, 824 (1927).

(4) Private communication to the junior author.

(5) (a) Lang, *Schweiz. Apoth. Ztg.*, **70**, 521–523 (1932); (b) Alther, *ibid.*, **70**, 615–618 (1932); *Chem. Abstracts*, **27**, 2532 (1933).

have been popular domestic remedies, having been used for a remarkably extensive list of ailments. Concerning the species *Sarothra gentianoides* L. (*H. sarothra* Michx.), one authority[6] records it as "a much used laxative, alterative, and vulnerary, under the names of Pineweed, False St. John's Wort, Orange Grass and Nitweed."

In the summer of 1923, the junior author, working with Dr. E. R. Miller at the Auburn (Ala.) Experiment Station, made a preliminary examination of a volatile oil obtained from *Sarothra gentianoides* L. but, due to the resignation of the junior author from the staff of the Experiment Station and the death of Dr. Miller, this investigation was suspended until a few years ago, when it was resumed as a coöperative undertaking by the chemical laboratories of Lenoir Rhyne College and Columbia University.

Collection and Distillation of the Plant.—The material used was collected in late August and early September, in the years 1925–1929, inclusive, and mostly in the neighborhood of Hickory, Catawba County, North Carolina.

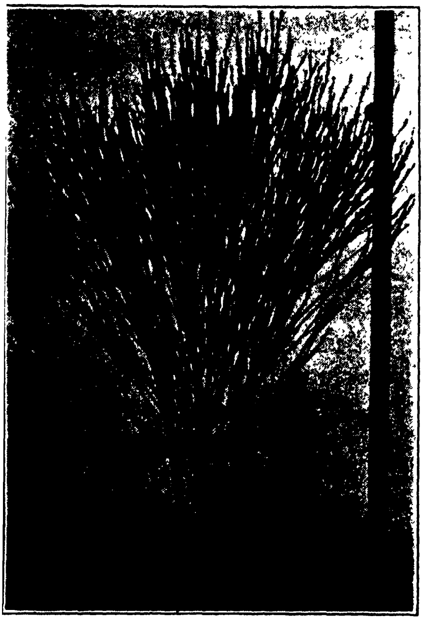

Plate I.—*Sarothra gentianoides* L., in full bloom.

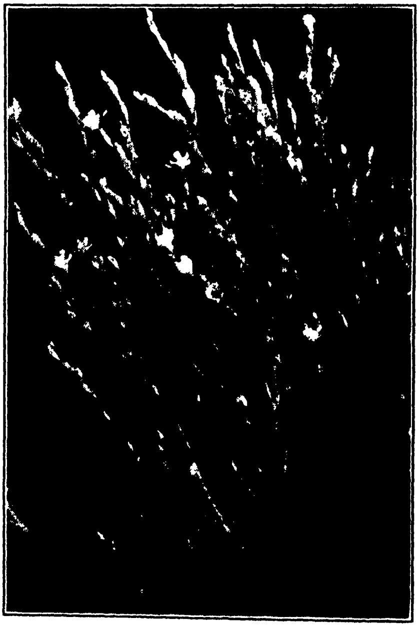

Plate II.—*Sarothra gentianoides* L., enlarged bushy top of plant, showing details of flowers.

The plants were pulled up by the roots, shaken to remove adhering dirt, examined carefully as to species, and all foreign matter removed. The entire fresh green herb, tops, stems and roots, was distilled with steam in

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(6) Millspaugh, *Am. Medicinal Plants*, I, Sec. 30 (1887).

100-lb. lots for periods of about three hours. The yield of volatile oil which separated in the distillate varied from 0.072 to 0.222%, for different years, due probably to different climatic conditions during the growing season. The general average yield of filtered oil, unwashed and undried, was approximately 0.1 to 0.2%, based on the weight of the fresh whole green plant.

The distillations carried out in 1925 are shown in Table I and it will be observed that the yields from the whole green plants, while not uniform, are consistently higher than the 1926 average of 0.098%. It is believed that this is due principally to the plentiful rainfall during the growing period, for we have noted that higher yields of oil are always obtained from the herbs gathered from low moist meadow land. It is possible that the better yield of oil in 1925 (as compared with 1926) may have been influenced somewhat also by the fact that the 1925 distillations were carried out with smaller lots.

During the season of 1925, distillations were also made on different portions of the plants, both fresh and dry. On August 27, 49 lb. of the whole fresh green herbs was collected and the bushy tops cut off, and the two portions, tops and roots, distilled separately. The 49 lb. gave 41 lb., or 83.6% of tops, and 8 lb., or 16.4% of roots and coarse stems. The tops gave a yield of 50.4 g. of oil, and the roots and coarse stems only 1.7 g. Therefore, 96% of the oil is localized in the tops of the plants, representing 83% of the mature herb.

TABLE I

1925 DISTILLATIONS

Date	Material, lb.	Yield, g.	Yield, %
	(1) Whole Green Plants		
Aug. 26	156.0	103.0	0.145
Sept. 17	15.0	15.0	.220
Sept. 19	21.0	21.1	.222
		Av. % yield...	.196
	(2) Green Tops Alone		
Aug. 27	41.0	50.4	0.217
Sept. 2	67.0	103.2	.339
Sept. 18	15.0	21.7	.318
		Av. % yield...	.291
	(3) Dry Tops Alone		
Sept. 17	11.0	13.2	0.264
Sept. 17	10.0	8.3	.183
Oct. 8	9.0	12.3	.301
		Av. % yield...	.249

As mentioned above, the average yield of oil obtained from the harvest of 1926 was only 0.098%, probably because of the very hot dry summer.

During this same 1926 season, a quantity of material was allowed to dry from ten days to four weeks in a cool, dry shed, spread out in a thin layer so as not to heat. In this drying, the herbs lost about 70% in weight, as well as some of the volatile oil, so that when distilled the yield of oil averaged only 0.095%, calculated to the dry basis. The only marked difference between this oil and that distilled from the green plants was that it was darker and had a more pronounced pinene odor.

An acre of plants was raised from seed sown in the spring of 1926 and harvested in August, 1927, but the yield of oil was no better than from the wild herb growing under similar climatic conditions.

The largest amount of material collected in any one season was in 1929, when nearly two tons were distilled and approximately two liters of filtered oil obtained.

Examination of the Oil.—The oil used for the following examination was distilled from the entire green plants—tops, stems and roots. It was filtered, washed thoroughly with water and then dried over anhydrous sodium sulfate.

Its color lay in the Green-Yellow zone, between Normal Tones and Tint 1, of the Bradley Color Standard. Its odor was agreeable, recalling that of oranges, with a slightly balsamic suggestion. It was soluble in chloroform, carbon tetrachloride, ether or absolute alcohol. Cold concentrated sulfuric acid changed its color first to a yellow, then to a purple and finally to a dark red. Cold concentrated nitric acid changed it first to a yellow, then to a dark red, with dark particles floating at the junction of the two liquid layers. It was unaffected by concentrated hydrochloric acid either hot or cold. The only effect produced by glacial acetic acid was to dissolve the oil. Neither cold nor hot 3 N sodium hydroxide caused any change in the color of the oil. Neutral potassium permanganate solution, or an equal volume of a 5% solution of bromine in carbon tetrachloride, was instantly decolorized by the oil. At $-17°$ the oil did not congeal, but assumed a slight milkiness which cleared up at $+5°$.

The following constants were determined: d_{20}^{20} 0.7665, n_D^{20} 1.4262, $[\alpha]_D$ +6.39, A. V. 0.58, S. V. 4.43, Ester No. 3.85, S. V. after acetylation 17.35.

Fuchsine and phenylhydrazine tests showed the presence of only traces of aldehydes or ketones. Further, the tests for phenols indicated that they also were present only in minute amount, if at all.

Following a qualitative examination for various elements, a combustion was run on the oil with this result: C, 84.03; H, 14.75; O, 1.22.

It was obvious from these results that the oil must consist mainly of hydrocarbons.

Fractionation of the Oil.—After removal of phenols, aldehydes, ketones, acids and esters, by the usual methods, from 360 cc. of the original whole green oil, the residual oil was washed, dried over anhydrous sodium sulfate and distilled four times with a 4-bulb Young fractionating column. Table II records the results obtained, compared with the constants of the original oil itself.

An examination of this table will disclose several unusual features. In the first place, 70% of this hydrocarbon oil distilled below 150°, and over 60% between 145 and 150°. This fact, taken in conjunction with the exceptionally low density of the oil and the other constants already recorded for the whole green oil, made it seem most likely that Fractions 1, 2 and 3, consisted mainly of acyclic hydrocarbons. Further, it was very significant that the only common volatile oils, of known composition, whose sp. gr. are lower than that of the *Sarothra* oil, are those from *Pinus sabiniana* (d_{15}, 0.6962–0.6971) and *Pinus jeffreyi* (d_{15}, 0.695–0.711), both of which consist principally of *n*-heptane. The density of the *Hypericum perforatum* oil, mentioned at the beginning of this paper, was reported by Miller[8] as 0.8065 to 0.8180 at 15°.

TABLE II

	B. p., °C.	d^{20}_{20}	n^{20}_{D}	$[\alpha]_D$	No. cc.
Whole green oil		0.7665	1.4262	+6.39	360
Fraction 1	140–145° at 758 mm.	0.7265	1.4071	+ 4.05	25
Fraction 2	145–150° at 758 mm.	.7366	1.4129	+ 7.52	210
Fraction 3	40–60° at 8–10 mm.	.7687	1.4278	+18.96	33
Fraction 4	60–110° at 8–10 mm.	.8014	1.4453	+ 7.46	13
Fraction 5	110–125° at 8–10 mm.	.8927	1.4892	− 9.77	30
Fraction 6	125–140° at 8–10 mm.	.9073	1.4844	− 4.75	8
Residue	Above 125–140° at 8–10 mm.				15
				Total	334
				Loss in handling, etc.	26
					360

Inasmuch as Fraction 2 of the above table represented over 60% of the distillate, had the characteristic odor of the plant and obviously contained the major portion of the low-boiling constituent, preliminary qualitative experiments were conducted with it, as well as some elementary analyses. The results of these experiments and analyses, taken in conjunction with the physical constants noted in the table, indicated that the major constituent of this fraction was a paraffin, probably a nonane, mixed with some olefin, perhaps a nonene or decene.

Isolation and Identification of *n*-Nonane.—As our interest lay primarily in the isolation and identification of this paraffin, a larger quantity of the oil, freed as far as possible from oxygenated compounds by suitable treatment, was repeatedly distilled and a fraction b. p. 146–152° at 735 mm. was collected. This was washed with concentrated sulfuric acid as long as it colored the acid, then with concentrated nitric acid, followed by water, dilute sodium carbonate solution, and water again. After being dried over anhydrous sodium sulfate, it was refluxed for two hours over metallic sodium and then repeatedly fractionated over the same material, finally taking the cut which boiled at 148.5–149.5° (corr.) at 735 mm. A calculation based on Craft's formula, $dt = KT_{\mathrm{BO}}\ (760 - P)$, and assuming that the liquid is non-associated, gives a boiling range of 149.5–150.5° at 760 mm.

A number of fractionations, therefore, were carried out with the oil distilled in different seasons from the whole green plant, and yields of 14–20% were obtained of a fraction of this b. p. (149.5–150.5°).

TABLE III

	Sarothra nonane	*n*-Nonane
B. p. at 760 mm., °C.	149.5–150.5	149–151
F. p.,[7] °C.	−60	−51 to −53.68
Sp. gr.	0.7177 at 20/20	0.717–0.738
n^{25}_{D}	1.4025	1.4025–1.4165
$[\alpha]_D$	Inactive	Inactive
Heat of combustion[8]	1.488 Cal.	1.462 Cal.
Mol. wt.	129.9	128.2
C%	84.20	84.27
H%	15.74	15.73

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(7) This was carried out in the laboratory of Dr. H. D. Crockford, Department of Physical Chemistry, University of North Carolina, Chapel Hill, N. C., to whom we are most grateful.

(8) We owe this determination to the courtesy of Professor E. E. Randolph, Department of Chemical Engineering, North Carolina State College, Raleigh, N. C.

Bearing in mind the fact that nearly 60% of the whole green oil distilled at temperatures not exceeding 150°, and that the narrow *n*-nonane cut (b. p. 149.5–150.5°) amounted to 14–20%, a conservative estimate would be that the original oil from the whole green plants contains at least 20% of *n*-nonane.

The carefully purified fraction referred to above, b. p. 148.5–149.5° at 735 mm., or 149.5–150.5° at 760 mm., was optically inactive, and in all its chemical reactions (potassium permanganate, bromine solutions, etc.) behaved like a paraffin hydrocarbon. The product was analyzed and various constants determined.

Table III gives the results side by side with those which appear in the literature (or are calculated).

Synthesis of *n*-Nonane.—As a further check upon the identity of the paraffin hydrocarbon isolated from the *Sarothra* oil, *n*-nonane was synthesized for purposes of comparison, by the method of Clarke and Adams,[9] condensing *n*-heptaldehyde first with ethylmagnesium bromide, hydrolyzing the product to the nonanol, converting this into the corresponding iodide, removing hydriodic acid from the latter by the action of strong alcoholic potassium hydroxide and catalytically reducing the nonene to nonane.

The synthetic *n*-nonane so obtained possessed the following constants: b. p. 149.5–150.5° at 760 mm., d_{20}^{20} 0.712, f. p. −51°, n_D^{25} 1.4055. In other respects it likewise appeared to be identical with the nonane isolated from the *Sarothra* oil. No change in boiling point could be detected when the two were mixed.

Other Hydrocarbons Present in the Oil.—Having isolated and identified the *n*-nonane in Fraction 2 of Table II, this same fraction was examined for olefins, inasmuch as its behavior with potassium permanganate and with bromine indicated clearly the presence of unsaturated hydrocarbons.

A portion of the oil was oxidized by potassium permanganate, the alkaline solution, filtered from precipitate and separated from unoxidized oil, acidified with dilute sulfuric acid and the acid solution distilled with steam. The silver salt prepared from the distillate contained 41.65% silver (average of four determinations), as compared with 41.67% silver in silver caprylate.

From the same distillate the sodium salt of the acid was prepared, and its aqueous solution exhibited a levo rotation of $[\alpha]_D$ −15.8°.

From another portion of Fraction 2, oxidized by chromic acid, an acid was obtained whose silver salt contained 52.19% silver. Silver valerate contains 51.64% silver.

The two acids isolated as oxidation products of Fraction 2, hence, seem to be valeric and active caprylic. These acids could have been formed either from a single tridecene, carrying its olefin bond between carbons 5 and 6, or from 2 different olefins, one a pentene and the other an octene. The latter is the more likely, in view of the physical properties of Fraction 2, the identification of caprylic acid in the whole green oil, and the fact that octene, C_8H_{16} (b. p. 123–124°; *d* 0.7275; n_D 1.4066), is the only olefin which has been detected in essential oils.

Preliminary tests indicate that the higher-boiling fractions shown in Table II are probably made up mainly of terpenes and sesquiterpenes, but this part of the investigation is still unfinished.

Oxygenated Constituents of the Oil.—Preliminary experiments were carried out also on the oxygenated constituents of the oil. Although the amount of material available was in most cases insufficient for conclusive results, these experiments are recorded for the benefit of other workers and because it is uncertain when this investigation can be resumed.

Reference to Table II showed that these constituents could not total more than 16.5% and, as noted above, the elementary analysis of the original oil disclosed only 1.22% (by difference) of total oxygen.

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[9] Clarke and Adams, THIS JOURNAL, 37, 2536 (1915).

Free Acids.—After shaking 750 cc. of the whole green oil with excess of a 3% sodium bicarbonate solution, the aqueous solution was separated, concentrated, acidified with dilute sulfuric acid, extracted with ether and the ether extract evaporated. The residual dark brown oil, of hircin odor, was dissolved in dilute sodium hydroxide and the silver salt prepared therefrom. This salt darkened and apparently suffered some decomposition on drying, which would make the analytical figures for silver too high. Ignition of the dry salt showed the presence of 49.63% of silver. The silver content of silver valerate is 51.64%, and of silver caproate 48.39%. The presence of caproic acid, therefore, is indicated.

Esters.—The saponification value (4.43) determined on the original oil showed the presence of a small percentage of ester. Some of the oil, therefore, after removal of phenols, aldehydes, ketones and free acids, was saponified with $N/2$ alcoholic potassium hydroxide. The alkaline solution was separated, concentrated, acidified with dilute sulfuric acid, and the acid solution distilled with steam. The distillate had an acid reaction and yielded a silver salt containing 41.69% of silver. The silver salt of caprylic acid contains 41.67% of silver.

Alcohols.—From Fraction No. 5, Table II, there was prepared, by the method of Wallach,[10] a nitroso chloride, which melted at 106.5°. The melting point recorded in the literature for the nitroso chloride of *l*-α-terpineol is 107–108°, and the odor and other properties of this fraction resembled those of liquid α-terpineol.

The constants noted in Table II for Fraction No. 6 corresponded fairly well with those of geraniol. Some of this fraction, hence, was oxidized by a chromic acid mixture, as recommended by Beckmann,[11] and the odor of citral was immediately evident, and the oily product behaved toward the Schiff reagent like citral itself.

Phenols.—Free acids were removed from the oil by agitation with dilute aqueous sodium bicarbonate. The undissolved oil was separated, extracted with a 3% potassium hydroxide solution, the alkaline extract acidified with dilute sulfuric acid and shaken with ether. Evaporation of the ether extract left a small quantity of a brownish residue, of vaseline-like consistency, from which a 3,5-dinitrobenzoate, m. p. 207° (uncorr.), was prepared by the method of Phillips and Keenan.[12]

Aldehydes.—After removal of acids and phenols, the oil was shaken with a 40% sodium bisulfite solution, the bisulfite extract separated and hydrolyzed by boiling with sodium carbonate, and the liberated aldehyde collected with ether. Removal of ether left a very small quantity of an oil, which gave a deep red with the Schiff reagent, and yielded a crystalline semicarbazone, m. p. 105–106° (uncorr.), when dissolved in 30 parts of glacial acetic acid and treated with a solution of 4 parts of semicarbazide hydrochloride in a little water, a *P*H at which ketones do not form semicarbazones so readily.

It is worthy of note that the melting point of *n*-caproic aldehyde (*n*-hexanal) semicarbazone has been reported as either 106°,[13] or 114.5–115°.[14]

Ketones.—A qualitative test on the original oil indicated the presence of a trace of ketone. A small sample of the oil, from which acids, phenols, aldehydes, etc., had been removed, as described above, was treated with a solution prepared from 50 g. of semicarbazide hydrochloride, 50 g. of sodium acetate, a small amount of water and sufficient ethyl alcohol to make a homogeneous mixture. After standing for three days, some crystals separated which, after recrystallization from alcohol, melted at 231–232° (uncorr.). Camphor semicarbazone melts at 236–238°. The amount of material we had available was not enough for its positive identification.

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[10] Wallach, (a) *Ann.*, **277**, 120 (1893); (b) **360**, 90 (1908).

[11] Beckmann, *ibid.*, **250**, 325 (1889).

[12] Phillips and Keenan, THIS JOURNAL, **53**, 1924 (1931).

[13] (a) Bagard, *Bull. soc. chim.*, [4] **1**, 319 (1907). (b) McRae and Manske, *J. Chem. Soc.*, 488 (1928).

[14] *Schimmel's Ber.*, Apr., 79 (1913).

Summary

1. The volatile oil of *Sarothra gentianoides* L. consists largely of liquid acyclic hydrocarbons, of which at least 20% is *n*-nonane, a compound which has not hitherto been found in nature.

2. In addition to *n*-nonane, there is evidence of the presence of the following: a low-boiling optically active olefin (probably an octene), unidentified terpenes and sesquiterpenes, α-terpineol, geraniol, traces of phenols, aldehydes and ketones, caproic acid and a caprylic ester.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE MALLINCKRODT CHEMICAL WORKS]

Preparation and Dehydration of 4,4-Dimethylpentanol-2 (Methylneopentylcarbinol)

BY FRANK C. WHITMORE AND AUGUST H. HOMEYER[1]

The dehydration of dimethylneopentylcarbinol[2] and of methylethylneopentylcarbinol[3] gives olefins without rearrangement and with dehydration chiefly from the smaller groups. The neopentyl group shows little tendency to supply the proton in the dehydrations. The acid splitting of a C–C linkage in certain olefins having a neopentyl group attached to the ethylenic carbon has been observed.[4] Methyl neopentyl ketone reacts with sodium hypobromite as if it enolized exclusively from the methyl group.[5] Moreover, neopentylethylene adds hydrogen bromide entirely contrary to Markownikoff's rule.[6] In a further study of the neopentyl group, methylneopentylcarbinol has been prepared and dehydrated. Contrary to expectation the dehydration took place mainly from the neopentyl rather than the methyl group, the chief product being 4,4-dimethylpentene-2. No product of any rearrangement was detected.

4,4-Dimethylpentene-2 has been reported by Favorsky and Alexeeva[7,8] who gave its boiling point as 84–86°. Edgar, Calingaert and Marker[9] found that dehydration of 4,4-dimethylpentanol-3 gave a mixture of 4,4-dimethylpentene-2 and rearranged olefins. Boord and Schurman[10] pre-

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[1] Mallinckrodt Research Fellow.

[2] Unpublished results, Whitmore and Wrenn.

[3] Whitmore and Laughlin, THIS JOURNAL, **55**, 3732 (1933).

[4] Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).

[5] Homeyer, Whitmore and Wallingford, *ibid.*, **55**, 4209 (1933).

[6] Unpublished results, Whitmore and Homeyer.

[7] Favorsky and Alexeeva, *J. Russ. Phys.-Chem. Soc.*, **50**, 557–570 (1918).

[8] Favorsky and Alexeeva, *C. A.*, **18**, 1466 (1924); *Chem. Zentr.*, III, 998 (1923).

[9] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1487 (1929).

[10] Boord and Schurman, Paper before the Division of Organic Chemistry, American Chemical Society, Washington, D. C., March 28, 1933.

pared 4,4-dimethylpentene-2 by dehydration of 4,4-dimethylpentanol-3 by the methyl xanthate method.

Experimental

Preparation of 4,4-Dimethylpentanol-2.—A total of 746 g. of 4,4-dimethylpentanone-2 was reduced[11] in twelve runs in moist benzene solution with sodium. The product was distilled through an 85 × 2.1 cm. packed column.[12] The fore-run from each distillation was used in the next reduction. The yield was 548 g., 72%; b. p. 137–137.5° (736 mm.); $n^{20}_{\rm D}$ 1.4188; d^{20}_4 0.8115; MR. found 36.12, calcd. 36.17.

The residue was 176 g. corresponding to 23% of the original ketone. Distillation through a 70 × 1 cm. indented column showed it to be the pinacol, 2,2,4,5,7,7-hexamethyl-octanediol-4,5: b. p. 98–100° (2–3 mm.); m. p. 34–36°. It crystallized very slowly; the index of refraction taken soon after distillation was $n^{20}_{\rm D}$ 1.461. *Anal.* Calcd. for $C_{14}H_{30}O_2$: C, 73.0; H, 13.1. Found: C, 72.6; H, 13.4. The rearrangement of this pinacol is being studied.

Derivatives of 4,4-Dimethylpentanol-2.—α-Naphthyl urethan, from petroleum ether, m. p. 86.5–87°. 3,5-Dinitrobenzoate, from dilute alcohol, m. p. 95.2–95.7°. The carbamate was prepared by converting the carbinol to the chloroformic ester with phosgene and then treating it with aqueous ammonia; m. p. 71°. *Anal.* Calcd. for $C_8H_{17}O_2N$: N, 8.81. Found: N, 8.82. The acetate distilled at 92–92.5° (90 mm.); $n^{20}_{\rm D}$ 1.4071; d^{20}_4 0.8563; MR. found 45.44, calcd. 45.30. The *tert*-butyl acetate distilled at 92–94° (7–8 mm.), $n^{20}_{\rm D}$ 1.4195. Chloral mono-(methylneopentylcarbinyl)-acetal was prepared by adding 12 g. of pure methylneopentylcarbinol to 16 g. of Eastman anhydrous chloral. An exothermic reaction occurred. On the following day the product was washed with three 50-cc. portions of water and dried over calcium chloride. The product was a colorless oil, heavier than water, $n^{20}_{\rm D}$ 1.459. Distillation was not attempted.

Dehydration of 4,4-Dimethylpentanol-2.—Two hundred and fifteen grams of the carbinol was mixed with 5.5 cc. of 100% sulfuric acid. The mixture was added to the distilling flask in 40–50 g. portions and dehydrated by distilling through a 91 × 1.4 cm. packed column.[12] Distillation was regulated by controlling the rate of heating and take-off so that the head temperature did not exceed 80°. Twenty-three cc. of water was separated from the distillate. The product was washed with sodium bicarbonate solution, dried over 5 g. of potassium carbonate and fractionated through the 91 × 1.4 cm. column at 739 mm. using a reflux ratio of 10:1.

Fraction	B. p., °C.	$n^{20}_{\rm D}$	d^{20}_4	Wt., g.	MR. found
1	74–75.3	1.3970	0.6885	41	34.31
2	75.3–75.6	1.3970	.6892	65	34.28
3	75.6–76.2	1.3981	.6903	42	34.31

The yield of olefins was 148 g. or 82%. The residue was 36 g., consisting chiefly of the unchanged carbinol. The calculated molecular refraction of the heptenes is 34.06 (Eisenlohr's values). Similar results were obtained in another experiment.

4,4-Dimethylpentene-1, b. p. 72.35° (760 mm.), $n^{20}_{\rm D}$ 1.3911, has been prepared in this Laboratory.[6] We are indebted to C. E. Boord for the properties of 4,4-dimethylpentene-2, b. p. 76.0–76.1° (760 mm.), $n^{20}_{\rm D}$ 1.3986. From the refractive indexes it is estimated that the olefin mixture contained 82% of 4,4-dimethylpentene-2 and 18% of 4,4-dimethylpentene-1.

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(11) Whitmore and Krueger, THIS JOURNAL, 55, 1531 (1933).

(12) Whitmore and Lux, *ibid.*, 54, 3451 (1932).

Ozonolysis.—Analysis of the olefin mixture by ozonolysis[13] was difficult because the ozonide was dangerously explosive. Decomposition by a boiling suspension of zinc dust was accompanied with foaming.

Formaldehyde was identified by the resorcinol-sulfuric acid test, by the Rimini-Schryver[14] test, and by its condensation product with dimethyldihydroresorcinol,[15] m. p. 185–187°. The yield of formaldehyde as determined by iodimetric titration was 5.6%.

Acetaldehyde was isolated to the extent of 25.4% as acetaldehyde–ammonia, m. p. 90°. It was also identified by the Leys test.[16]

The oil isolated from ozonolysis of 58 g. of olefin amounted to 35 g. It contained both aldehydes and acids and separation even by repeated fractionation was not satisfactory. The aldehydes were oxidized to acids by excess alkaline potassium permanganate. The acids were separated as well as possible by several distillations and converted to the amides. Trimethylacetamide, m. p. 154–155°, was obtained after four crystallizations from ethyl acetate by adding petroleum ether. The mixed melting point with a known sample showed no depression. *Tert*-butylacetamide was not obtained pure. After repeated crystallizations it melted at 124–125° and a mixture with a known sample, m. p. 131°, melted at 126–127°. A mixture of *tert*-butyl acetamide (7.5 mg.) with trimethylacetamide (5.0 mg.) melted at 123–125°.

A search for acetone in the aqueous products of ozonolysis by attempting to obtain its dibenzylidene derivatives failed. The method was checked successfully with a known 3% solution of acetone.

Summary

Reduction of methyl neopentyl ketone in moist benzene solution with sodium gave 4,4-dimethylpentanol-2 (72% yield) and 2,2,4,5,7,7-hexamethyloctanediol-4,5. Dehydration of the carbinol gave 4,4-dimethylpentene-2 and 4,4-dimethylpentene-1 in the ratio 4.5:1.

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(13) Whitmore and Church, THIS JOURNAL, **54**, 3712 (1932).

(14) Schryver, *J. Chem. Soc.*, **98** ii, 334 (1910).

(15) Weinberger, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 365 (1931).

(16) Leys, *J. pharm. chim.*, [6] **22**, 107 (1905); *Bull. soc. chim.*, [3] **33**, 1316 (1905); *Chem. Zentr.* II, 855 (1905).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

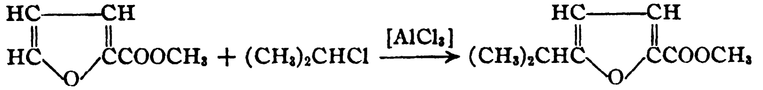
Super-Aromatic Properties of Furan. II. The Friedel-Crafts Reaction

BY HENRY GILMAN AND N. O. CALLOWAY

Introduction

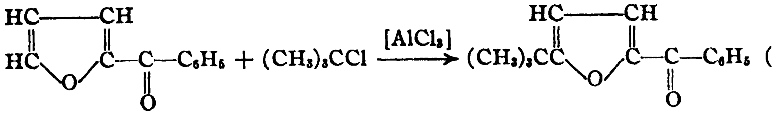
The scission of furylphenyllead and furylthienyllead compounds by hydrogen chloride has been presented as evidence in support of the super-aromatic nature of furan.[1] In a by-and-large definition of aromatic compounds and aromatic properties,[1] the Friedel-Crafts reaction is important historically as one of a small number of transformations peculiarly characteristic of aromatic compounds.[2] We now know that this reaction is shown not only by unsaturated aliphatic compounds, but also apparently by some saturated aliphatic compounds.[3] However, the reaction is still considered, in the aggregate, as a transformation that is typical of aromatic compounds.

Not all aromatic compounds undergo the Friedel-Crafts reaction. This is particularly true of many benzenoid types having a meta-orienting substituent. One of the most striking illustrations is nitrobenzene, which finds application as a solvent or medium for some Friedel-Crafts reactions. Not only do furan and 2-methylfuran undergo acylation,[4] but we have found that some so-called negatively substituted furans also participate in Friedel-Crafts reactions. Methyl 2-furoate, for example, undergoes ready alkylation and acylation under customary conditions, and the related methyl benzoate does not show these reactions. Substitution takes place in the α-position.



(I)

The same type of condensation occurs with 2-furoic acid and with 2-furyl phenyl ketone. The reaction with 2-furyl phenyl ketone is particularly significant because it presents an opportunity to observe the relative aromaticities of a 2-furyl and a phenyl nucleus in a symmetrical compound. Condensation takes place only in the furyl nucleus.



(II)

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[1] Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932).

[2] Victor Meyer, "Die Thiophengruppe," Brunswick, 1888, p. 276.

[3] Krapivin, *Bull. Soc. Imp. Nat. Moscow*, **1**, 176 (1908); v. Braun and Kuhn, *Ber.*, **45**, 1267 (1912), and **60**, 2557 (1927); Norris and Couch, THIS JOURNAL, **42**, 2329 (1920); Wieland and Bettay, *Ber.*, **55**, 2246 (1922); Nenitzescu and Ionescu, *Ann.*, **491**, 189 (1931); Hopff, *Ber.*, **64**, 2739 (1931), and **65**, 482 (1932); Unger, *ibid.*, **65**, 467 (1932).

[4] Reichstein, *Helv. Chim. Acta*, **13**, 356 (1930).

This preferential nuclear substitution, and the condensations with methyl furoate but not with methyl benzoate, together with the fact that benzene can be used as a medium for some Friedel–Crafts reactions of furan are advanced as supporting evidence for the concept that furan has super-aromatic properties.

As previously mentioned,[1] some benzenoid types are apparently more aromatic than others. This is especially true of benzene derivatives having amino and phenolic or substituted amino and substituted phenolic[4] groups. In accordance with this general principle it has been found that methyl anisate (p-$\text{CH}_3\text{OC}_6\text{H}_4\text{COOCH}_3$), unlike methyl benzoate, undergoes the Friedel–Crafts reaction. Also, the correlation of the α-positions in naphthalene with the α-positions in furan[5] finds support in the observation that the Friedel–Crafts reaction takes place with ethyl α-naphthoate.

Constitution of Products.—The structure of 5-*tert*-butyl-2-furyl phenyl ketone was established by comparison with the product obtained by interaction of 5-*tert*-butyl-2-furoyl chloride with benzene and aluminum chloride.

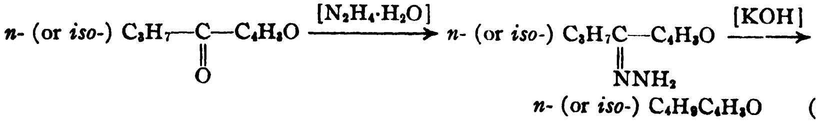
The ketones obtained from furan and acid chlorides were identical with those prepared from 2-furylmercuric chloride and the acid halides, and from 2-furonitrile and the appropriate Grignard reagent.[6]

The alkylation products of methyl 2-furoate were somewhat unusual in the sense that the alkyl group appeared to undergo rearrangement so that, for example, each of the four butyl chlorides (as well as butylene) gave some of the same product: namely, methyl 5-*tert*-butyl-2-furoate. The structure of this compound was established by a process of exclusion. The *n*-butyl-, isobutyl-, and *sec*-butyl derivatives were synthesized and shown to be unlike the compound obtained by the Friedel–Crafts reaction which was characterized as follows

$$\text{5-C}_4\text{H}_9\text{C}_4\text{H}_2\text{OCOOCH}_3\text{-2} \xrightarrow{[\text{HOH}]} \text{5-C}_4\text{H}_9\text{C}_4\text{H}_2\text{OCOOH-2} \xrightarrow{[-\text{CO}_2]}$$

$$\text{5-C}_4\text{H}_9\text{C}_4\text{H}_3\text{O} \xrightarrow[\text{[NaAc]}]{[\text{HgCl}_2]} \text{5-C}_4\text{H}_9\text{C}_4\text{H}_2\text{OHgCl-2} \qquad \text{(III)}$$

This mercurial as well as the butylfuran from which it was prepared were shown to be unlike the other three possible 5-butyl-2-furylmercuric chlorides and the corresponding 2-butylfurans. The *n*-butyl- and isobutylfurans were synthesized as follows



$$n\text{- (or }iso\text{-) C}_3\text{H}_7\text{—}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—C}_4\text{H}_3\text{O} \xrightarrow{[\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}]} n\text{- (or }iso\text{-) C}_3\text{H}_7\underset{\underset{\text{NNH}_2}{\|}}{\text{C}}\text{—C}_4\text{H}_3\text{O} \xrightarrow{[\text{KOH}]} n\text{- (or }iso\text{-) C}_4\text{H}_9\text{C}_4\text{H}_3\text{O} \qquad \text{(IV)}$$

(IV)

The following reactions illustrate the synthesis of *sec*-butylfuran

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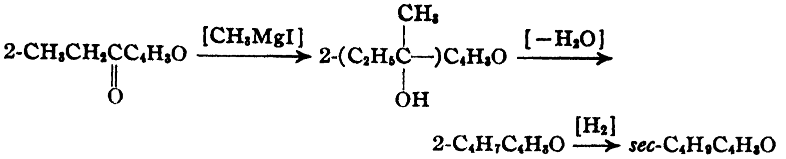
(5) Gilman and Wright, *Chem. Rev.*, **11**, 330 (1932).

(6) Asahina and Murayama, *Arch. Pharm.*, **252**, 435 (1914).



$$2\text{-}CH_3CH_2\underset{\underset{O}{\|}}{C}C_4H_3O \xrightarrow{[CH_3MgI]} 2\text{-}(C_2H_5\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}\text{—})C_4H_3O \xrightarrow{[-H_2O]}$$

$$2\text{-}C_4H_7C_4H_3O \xrightarrow{[H_2]} sec\text{-}C_4H_9C_4H_3O \qquad \text{(V)}$$

This sequence of reactions is related to that used recently[7] for the preparation of 2-isopropylfuran $C_4H_3OCOOC_2H_5 \xrightarrow{[CH_3MgI]} C_4H_3OC(CH_3)_2OH \xrightarrow{[-H_2O]} C_4H_3OC(CH_3){=}CH_2 \xrightarrow{[H_2]} C_4H_3OCH(CH_3)_2$. Our isopropylfuran is identical with this compound, and thus gives added support to the generalization[5] that nuclear substitution occurs in an α-position if one be available.

Methyl chloride gave a dithio ester, as a consequence of interaction with the carbon disulfide;[8] ethyl chloride and ethyl bromide apparently undergo a reaction like that observed with methyl chloride; both *n*-propyl and isopropyl chloride gave the same isopropyl derivative [methyl 5-isopropyl-2-furoate], so that smooth alkylation of methyl furoate really starts with the propyl halides; and the amyl and hexyl derivatives, prepared from *n*-amyl chloride and *n*-hexyl bromide, probably are branched chain types by analogy with the formation of *tert*-butylfuran from each of the four isomeric butyl halides.

The structures of the acylation products of methyl furoate were established as follows, using acetic anhydride as a type

$$C_4H_3OCOOCH_3 + (CH_3CO)_2O \xrightarrow[\text{[SnCl}_4]]{\text{[FeCl}_3\text{ or]}} CH_3COC_4H_2OCOOCH_3 \xrightarrow{[HOH]}$$

$$CH_3COC_4H_2OCOOH \xrightarrow{[-CO_2]} 2\text{-}CH_3COC_4H_3O \qquad \text{(VI)}$$

The chief problem in determining the constitution of a monoacylated nuclear substituted product of a di-α-substituted furan having like substituents concerns the integrity of the furan nucleus. The nucleus is not cleaved significantly in a Friedel–Crafts reaction. This was established in the case of the acetylated 2,5-dimethylfuran by preparing the same compound from 2,5-dimethylfurylmercuric chloride and acetyl chloride. The resulting 2,5-dimethyl-3-furyl methyl ketone was prepared earlier by the condensation of succinic acid and acetic anhydride with zinc chloride.[9]

An anomalous reaction takes place between 2-furfural and isopropyl chloride. The product is not 5-isopropyl-2-furfural, but appears to be a related dihydrofuran or possibly a compound formed by nuclear cleavage.

Experimental Part

2-Furyl Phenyl Ketone and *tert*-Butyl Chloride.—Eight grams (0.05 mole) of 2-furyl

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(7) Reichstein, Zschokke, Gehring and Rona, *Helv. Chim. Acta*, **15**, 1118 (1932).

(8) Jorg, *Ber.*, **60**, 1466 (1927).

(9) Magnanini and Bentivoglis, *Gazz. chim. ital.*, **24**, I, 435 (1894).

phenyl ketone in carbon disulfide were brought into reaction with *tert*-butyl chloride and aluminum chloride under the conditions described later [see "Alkylation of Methyl 2-Furoate"], with the exception that no ice-bath was used. The resulting 5-*tert*-butyl-2-furyl phenyl ketone (30% yield) is unusually stable: b. p. 180–182° (20 mm.) and 187–189° (22 mm.); d_{25}^{25} 1.065; n_{D}^{25} 1.5665.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.94; H, 7.06. Found: C, 79.06; H, 7.54.

The same compound was obtained in a 70% yield by condensing 5-*tert*-butyl-2-furoyl chloride (0.1 mole), aluminum chloride (0.1 mole) and 100 cc. of benzene.

The 5-*tert*-butyl-2-furoyl chloride was obtained (51% yield) by refluxing 5-*tert*-butyl-2-furoic acid with thionyl chloride; b. p. 220°; d_{25}^{25} 1.108; n_{D}^{25} 1.5091.

Anal. Calcd. for $C_9H_{11}O_2Cl$: Cl, 19.03. Found: Cl, 19.37.

2-Furfural and Isopropyl Chloride.—In an experiment with 0.5 mole of furfural, 0.5 mole of isopropyl chloride, and 0.6 mole of aluminum chloride in carbon disulfide no external cooling was applied. There was a marked evolution of hydrogen chloride, and but very little charring was noted. Subsequent to hydrolysis of the reaction mixture, the carbon disulfide layer was washed first with water and then with sodium acetate. Then 200 cc. of a saturated solution of sodium acetate was added, and the resulting aldehyde steam distilled. This aqueous distillate was extracted with the carbon disulfide which first distilled over, washed with sodium bicarbonate, dried over sodium sulfate, and the aldehyde, after removing carbon disulfide, was distilled under reduced pressure.

The yield was 8 g. of aldehyde distilling at 101–103° (21 mm.); d_{25}^{25} 1.023; n_{D}^{25} 1.5041. The constitution of this aldehyde has not yet been established, but it appears to be a dihydrofuran derivative.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.52; H, 8.64. Found: C, 69.49; H, 8.38.

The aldehyde is relatively unstable and darkens on atmospheric exposure. When oxidized by alkaline silver oxide it gives a carboxylic acid which is unlike 5-isopropyl-2-furoic acid.[7] This new acid, which may be a dihydro-isopropylfuroic acid or a ring scission product, melts at 76–77° when crystallized from 40% ethyl alcohol. In an orienting experiment the supposed dihydroisopropylfuroic acid was heated with phosphorus pentachloride to remove two hydrogens and give the known 5-isopropyl-2-furoic acid; however, the original acid was recovered after alkaline hydrolysis. *Neutralization equivalent.* Calcd., 156; found, 155.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.49; H, 7.75. Found: C, 61.71; H, 7.45.

The semicarbazone of the aldehyde melts at 174–176° when crystallized from 30% alcohol, and its analysis agrees for a dihydro derivative.

Anal. Calcd. for $C_9H_{15}O_2N_3$: C, 54.79; H, 7.66. Found: C, 54.65; H, 7.42.

The unknown aldehyde was condensed with sodium acetate and acetic anhydride to give a 40% yield of an acid which analyzes for a dihydroisopropylfurylacrylic acid. This acid melts at 102–103° when crystallized from water and alcohol. *Neutralization equivalent.* Calcd., 182.1; found, 180.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.89; H, 7.74. Found: C, 65.93 and 65.93; H, 7.75 and 7.66.

Furan and Acid Chlorides.—To 26.6 g. (0.2 mole) of aluminum chloride in 250 cc. of carbon disulfide contained in a three-necked flask provided with a mechanical stirrer was added 0.2 mole of the acid chloride. The flask and contents were then chilled with an ice-bath. Furan (0.2 mole), prepared in accordance with recent directions,[10] contained in 50 cc. of carbon disulfide was added dropwide over a twenty-five minute period;

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[10] Gilman and Lousinian, *Rec. trav. chim.*, **52**, 156 (1933).

the mixture turned dark brown, and after about one-third of the furan had been added copious quantities of hydrogen chloride were evolved. Stirring was continued for fifteen minutes in the ice-bath, and then for ten minutes at room temp., after which the mixture was poured upon 300 g. of cracked ice, and steam distilled; the distillate was made alkaline with potassium hydroxide, extracted with ether, dried over sodium sulfate, and the alkyl 2-furyl ketone distilled under reduced pressure. The data are given in Table I.

TABLE I

ALKYL 2-FURYL KETONES FROM FURAN AND ACID CHLORIDES

	Alkyl 2-furyl ketone	RCOCl used	Yield, %	B. p. (mm.), °C.	d_{25}^{25}	n_D^{25}
1	Ethyl	*n*-Propionyl	36.3	78–80 (17) m. 27–28°	....	....
2	*n*-Propyl	*n*-Butyryl	51.8	95–97 (19)	1.041	1.4922
3	Isopropyl	Isobutyryl	45.3	86–87 (18)	1.032	1.4888
4	*n*-Butyl	*n*-Valeryl	23	108–109 (18)	1.012	1.4900
5	*n*-Amyl	*n*-Caproyl	39	116–119 (16)	0.9954	1.4864

	Analyses, %				Semicarbazone and analyses				
	Calcd.		Found			Carbon		Hydrogen	
	C	H	C	H	M. p., °C.	Calcd.	Found	Calcd.	Found
1	67.71	6.50	67.65	6.66	188–190	(a)		(a)	
2	69.52	7.30	70.02	7.40	190	(a)		(a)	
3	69.52	7.30	69.45	7.63	...	....		....	
4	71.01	7.96	71.32	8.15	158–159	57.22	57.22	7.22	6.73
5	72.24	8.49	71.77	8.76	110–112	54.68	54.97	7.66	7.41

TABLE II

ALKYLATION OF METHYL 2-FUROATE

	Methyl 5-alkyl 2-furoate	Alkyl halide used	Yield, %	B. p. (mm.), °C.	d_{25}^{25}	n_D^{25}
1	5-Isopropyl-	*n*-Propyl chloride[b]	48	110–112 (20)	1.076	1.4851
2	5-*tert*-Butyl-	*n*-Butyl chloride[c]	45	110–114 (15)	1.037	1.4792
3	5-Amyl-	*n*-Amyl chloride	31	112–116 (13)	1.032	1.4804
4	5-Hexyl-	*n*-Hexyl bromide	57.1	132–136 (19)	1.016	1.4814

	Analyses, %				5-Alkyl-2-furoic acid and analyses				
	Calcd.		Found			Calcd.		Found	
	C	H	C	H	M. p., °C.	C	H	C	H
1	64.24	7.20	63.87	7.36	65–66	62.29	6.54	62.45	6.44
2	65.90	7.74	66.20	7.91	104–105	64.24	7.20	64.51	7.40
3	67.34	8.16	67.10	8.21	69.70	65.90	7.44	66.3	7.95
4	68.34	8.63	68.45	8.51	36–37	67.34	8.16	67.1	7.99

[a] These semicarbazones were prepared and analyzed by Asahina and Murayama.[8] [b] The yield of methyl 5-isopropyl-2-furoate from isopropyl chloride was 42%. [c] From 12.6 g. (0.1 mole) of methyl furoate, 0.1 mole of *tert*-butyl chloride, 0.12 mole of ferric chloride in place of aluminum chloride and 100 cc. of carbon disulfide there was isolated but two fractions: one of these (8 g.) was recovered methyl furoate and the other a 41.3% yield of methyl 5-*tert*-butyl-2-furoate. The yield of methyl 5-*tert*-butyl-2-furoate from isobutyl bromide was 66%; from *sec*-butyl bromide, 1.6%; and from *tert*-butyl bromide, 46%.

The several ketones were also prepared by interaction of 2-furyl-mercuric chloride and the appropriate acid chloride, in accordance with recent directions.[11] The ketones prepared by these two methods were identical, as established by mixed melting point determinations of the semicarbazones. The yields of alkyl 2-furyl ketones prepared from 2-furylmercuric chloride were as follows: ethyl, 24.2%; *n*-propyl, 18.1%; isopropyl, 14.5%; and *n*-amyl, 18%.

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[11] Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).

In accordance with Steinkopf's[12] directions for the preparation of 5-ethyl-2-thienyl ethyl ketone from ethylthiophene, propionyl chloride and phosphorus pentoxide, a reaction was attempted between furan, ethyl chlorocarbonate and phosphorus pentoxide. The furan was recovered practically quantitatively.

The difficulty in *alkylating* furan with *n*-butyl chloride, aluminum chloride and carbon disulfide or furan itself as a medium may be due in part to a coating which formed on the aluminum chloride.

Alkylation of Methyl 2-Furoate.—In these experiments 0.1 mole of methyl furoate and 0.1 mole of alkyl halide was added dropwise over a twenty-five minute period to 0.1–0.2 mole of aluminum chloride and 200 cc. of carbon disulfide contained in a three-necked flask provided with a mechanical stirrer and cooled by an ice-bath. A dark, viscous oil separated in each case leaving a clear supernatant liquid, and hydrogen chloride was evolved promptly with the lower halides but more slowly with the higher ones. When addition was complete, the ice-bath was removed and the mixture allowed to stand for twenty-four hours. Because the evolution of hydrogen halide is very slow with *n*-hexyl bromide, the ice-bath was removed directly after admixing the reactants. The reaction product was poured upon 500 g. of cracked ice with *vigorous* stirring to prevent extreme local heating, the solvent separated, and the aqueous layer extracted three times with 200-cc. portions of ether. The ether and carbon disulfide solutions were combined, washed with 200 cc. of water and then with 200 cc. of a saturated sodium bicarbonate solution, dried over sodium sulfate, and the heavy residual liquid (after removing the solvents) was fractionated in a Claisen flask with indentations. It was found desirable to fractionate at least three times in order to obtain a product which on hydrolysis would yield a solid acid; otherwise, oily acids are obtained which are very difficult to crystallize. In view of the difficulty of fractionation it appears altogether reasonable to conclude that isomeric 2-butyl esters were formed.

Hydrolysis was effected by heating 10 g. of the ester at 80° with a 20% solution of alcoholic potassium hydroxide for ten minutes. The mixture was then poured into 100 g. of cracked ice in 200 cc. of water, and acidified slowly by the addition, with stirring, of 50% iced sulfuric acid. Solution in cold dilute potassium hydroxide and reprecipitation with cold sulfuric acid is sometimes desirable. Crystallization is effected from an alcohol–water mixture. The yields on hydrolysis are in excess of 75%. Unnecessary heating should be avoided to prevent the precipitation of the acids as oils. The data are given in Table II.

The best method for the preparation of 5-*tert*-butyl-2-furoic acid is probably that one involving the use of isobutyl bromide. The actual reaction is completed in three hours (and the entire preparation in five hours); but one fraction is obtained and this distils at 110–116° (20 mm.) to give a 77% yield. Redistillation gives a 66% yield of ester distilling at 112–114° (20 mm.).

In the reaction with methyl chloride, the gas was bubbled into a mixture obtained by adding 63 g. or 0.5 mole of methyl furoate to 1 mole of aluminum chloride in 300 cc. of carbon disulfide. The reaction product yielded 35 g. of the original methyl furoate and 25 g. of a red viscous oil which when finally crystallized from an alcohol–water mixture melted at 102–103°. This experiment was checked. However, when petroleum ether (b. p. 30–60°) was used as a medium in place of carbon disulfide, only methyl furoate was isolated (65% recovery). The deep red compound is uncommonly stable under ordinary conditions, and the color was not discharged by heating for one hour with 30% hydrogen peroxide. The compound may be 5-carbomethoxy-2-carbodithiomethoxyfuran (5-$CH_3CO_2C_4H_2OCS_2CH_3$).

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[12] Steinkopf, *Ann.*, **430**, 105 (1923).

Anal. Calcd. for $C_8H_8O_3S_2$: S, 29.63. Found: S, 28.71 (by Carius), and 29.10 (by Parr bomb).

In an attempted alkylation of diethyl 2,5-furandicarboxylate with *n*-butyl chloride and aluminum chloride, the dibasic ester was recovered.

Sec-Butyl-2-furan from Ethyl 2-Furyl Ketone.—The ethyl furyl ketone (0.42 mole) was added slowly to methylmagnesium iodide and hydrolysis was effected by iced dilute acetic acid to give a 66.3% yield of methylethyl-2-furylcarbinol (Reaction (V)); b. p. 77–78° (19 mm.); d^{25}_{25} 1.023; n^{25}_{D} 1.4729.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.52; H, 8.64. Found: C, 68.90; H, 9.02.

The tertiary alcohol (0.34 mole) was dehydrated by refluxing with acetic anhydride (0.5 mole) for twenty minutes. The oil obtained subsequent to hydrolysis by iced potassium hydroxide, ether extraction and drying was fractionated. That part distilling at 145–150° was probably a mixture of the two possible furylbutylenes, and because of its relative instability was reduced at once by Adams' method to give the 2-*sec*-butylfuran distilling at 132–135°. This compound and its mercurial were analyzed (see Table III).

Alkylation of 2-Furoic Acid.—In an orienting experiment, 0.5 mole of furoic acid, 1 mole of aluminum chloride and 0.5 mole of *n*-butyl chloride were allowed to react in carbon disulfide. The oily product yielded 6% of 5-*tert*-butyl-2-furoic acid. This yield can be improved considerably, but the reaction with the ester is preferred because of the apparent greater ease of purifying the liquid ester mixture rather than the mixture of solid acids.

Alkyl-2-furans.—Decarboxylation of 10 g. quantities of the alkyl-2-furoic acids was effected by Johnson's procedure, using quinoline and copper bronze, the distillate being collected in iced 5% sulfuric acid. The alkylfurans were then recovered by the customary procedures.

Some alkyl-2-furans were prepared by the Wolff–Kischner procedure from the alkyl 2-furyl ketones by first heating the ketone and hydrazine hydrate in dry methyl alcohol, and then adding potassium hydroxide pellets and heating again until gas evolution ceased. The alkylfurans were characterized as their mercurials, *n*-propylfuran, for

TABLE III

2-ALKYLFURANS AND 5-ALKYL-2-FURYLMERCURIC CHLORIDES

	2-Alkylfurans	Method of preparation	Yield, %	B. p., °C.	d^{25}_{25}	n^{25}_{D}
1	2-*n*-Propyl-	Reduction of ketone	36	114–116	0.882	1.4410
2	2-Isopropyl-	Decarboxylation	55	106–109	.8771	1.4466
3	2-*n*-Butyl-	Reduction of ketone	53.8	137–138	.8983	1.4460
4	2-Isobutyl-	Reduction of ketone	32	123–127	.886	1.4425
5	2-*sec*-Butyl-	Reduction of 2-butenylfuran	.	132–135	....	....
6	2-*tert*-Butyl-	Decarboxylation	60	119–120	.8708	1.4380

	Analyses, %				5-Alkyl-2-furyl-mercuric chloride		
	Calcd.		Found			Hg analyses, %	
	C	H	C	H	M. p., °C.	Calcd.	Found
1	76.29	9.09	75.81	9.36	99	58.11	58.01
2	76.29	9.09	75.95	9.57	117–118	58.11	58.22
3	77.36	9.83	77.28	9.64	79–80	55.84	55.35
4	77.36	9.83	77 45	9 71	95–96	55.84	55.41
5	77.36	9.83	77.50	10.20	88	55.84	56.0
6	77.36	9.83	77.01	10.10	136–137	55.84	55.52

example, giving 5-*n*-propyl-2-furylmercuric chloride. The yields of mercurials prepared by the general method described recently[11] were about 35%. Data on the alkylfurans and their mercurials are contained in Table III.

Acylation of Furoic Esters.—In sharp contrast with the alkylation of methyl furoate, aluminum chloride appeared to be ineffective in a Friedel–Crafts reaction of the ester with acetic anhydride or acetyl chloride. It is possible that the quality of aluminum chloride has a marked effect in such condensations if one may judge by pronounced variations in yield in the reaction between furoic acid, benzene and aluminum chloride.[13] However, both ferric chloride and stannic chloride worked satisfactorily with acid anhydrides to introduce an acyl group in the α-position.

Ethyl 5-acetyl-2-furoate was prepared in 30% yield from 0.4 mole of ethyl furoate 0.4 mole of acetic anhydride, 0.8 mole of stannic chloride and 250 cc. of dry thiophene-free benzene. The fraction distilling between 125–170° (20 mm.) was crystallized from 80% alcohol to give the keto ester, which melted at 85–86°.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.31; H, 5.55. Found: C, 59.68; H, 5.97.

The corresponding keto acid, obtained by alkali hydrolysis of the ester, did not melt up to 230°, but decomposed gradually with blackening. *Neutralization equivalent.* for 5-acetyl-2-furoic acid: calcd., 154; found, 153.5. Decarboxylation of the keto acid by heating in the presence of copper bronze gave methyl 2-furyl ketone. This ketone was characterized by its semicarbazone (mixed m. p.).

Methyl 5-*n*-butyryl-2-furoate was prepared from methyl furoate, *n*-butyric anhydride and stannic chloride in benzene. The fraction distilling between 145–160° (20 mm.) when recrystallized from alcohol and water gave a 25% yield of keto ester melting at 67–68°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.19; H, 6.17. Found: C, 61.31; H, 6.20.

Hydrolysis of the ester gave 5-*n*-butyryl-2-furoic acid; m. p. 172°. *Neutralization equivalent.* Calcd., 182; found, 181.4. Decarboxylation of the keto acid gave *n*-propyl 2-furyl ketone which was characterized by its semicarbazone (mixed m. p.).

2,5-Dimethylfuran with Acetic Anhydride, Benzoyl Chloride and Benzoic Anhydride.[14]—The yield of 2,5-dimethyl-3-furyl methyl ketone from 2,5-dimethylfuran (0.14 mole), ferric chloride and acetic anhydride was 42%. The same compound (b. p. 94–96° (18 mm.); m. p. and mixed m. p. of oximes, 78°) was obtained in a 22% yield from 2,5-dimethyl-3-furylmercuric chloride[15] (0.05 mole) and acetyl chloride.

2,5-Dimethyl-3-furyl phenyl ketone was prepared in 7% yield from 2,5-dimethylfuran, benzoyl chloride, aluminum chloride, and carbon disulfide; in like yield from 2,5-dimethylfuran, benzoic anhydride, and ferric chloride and carbon disulfide; and in 29% yield when benzoic anhydride and stannic chloride were used in benzene; b. p. 140° (15 mm.), 152° (17 mm.); d_{20}^{20} 1.152; n_{D}^{25} 1.5602.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.96; H, 6.05. Found: C, 77.56 and 77.52; H, 6.30 and 6.32.

General Observations on the Stability of the Products.—The alkyl 2-furoates are relatively stable, but they often darken on standing. However, the α-alkylated alkyl furoates are quite stable and retain their water clear transparency or darken only to a golden-yellow upon standing for two years in the presence of air, which generally has a deleterious effect on many furan compounds. The opposite effect is observed with 2-alkylfurans which polymerize to a resinous yellow-brown solid on standing for a long period in an ice box, under conditions where furan itself is stable. These observations indicate that the stability is greatest when the two α-positions are occupied by certain

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(13) King, THIS JOURNAL, 49, 565 (1927), and private communication from Dr. E. J. King.

(14) These experiments were carried out by Nelson E. Sanborn.

(15) Kindly provided by Robert R. Burtner.

groups, and this finds support with some other di-α-substituted furans. The alkenyl furan polymerized overnight.

The 2-furyl ketones were of moderate stability, and gradually darkened. It is interesting to note that as they assumed a darkened color they developed a very pleasant odor. The agreeableness of this bouquet appears to increase with the lengthening of the alkyl group, and this applies both to the freshly prepared ketones as well as to those which had aged for several months.

The alkylated 2-furylmercuric chlorides were less stable than one might have expected. After three months they underwent significant decomposition to insoluble compounds containing a high percentage of mercury.

Methyl Anisate and Isopropyl Chloride.—From 0.075 mole of methyl anisate, 0.075 mole of isopropyl chloride, 0.15 mole of aluminum chloride and 225 cc. of carbon disulfide there was obtained a 33.6% yield of methyl 3-isopropyl-4-methoxybenzoate (assuming normal orientation); b. p. 162–165° (25 mm.); d^{25}_{25} 1.074; n^{25}_{D} 1.5236.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.15; H, 7.74. Found: C, 69.31; H, 8.19.

Hydrolysis by alcoholic potassium hydroxide gave an acid which when crystallized from alcohol and water melted at 162–163° with softening at 158°. *Neutralization equivalent.* Calcd., 194.1; found, 195, 195. *Methoxyl.* Calcd., 17.17; found, 16.74.

Ethyl α-Naphthoate with Isopropyl and *n*-Butyl Chlorides.—From 0.05 mole of ethyl α-naphthoate, 0.05 mole of isopropyl chloride, 0.1 mole of aluminum chloride and 215 cc. carbon disulfide there was obtained a 33% yield of ethyl isopropyl-α-naphthoate; b. p. 198–203° (20 mm.); d^{25}_{25} 1.077; n^{25}_{D} 1.5760.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.27; H, 7.51. Found: C, 79.15; H, 7.32.

Hydrolysis by alcoholic potassium hydroxide gave a mixture of acids which when crystallized from water and alcohol melted between 68–72°. The calcd. neutralization equivalent for $C_{14}H_{14}O_2$ is 214; found, 213.4. In a corresponding preparation using *n*-butyl chloride, an ethyl butyl-α-naphthoate was obtained; b. p. 230–235° (18 mm.); d^{25}_{25} 1.0131; n^{25}_{D} 1.5552.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.62; H, 7.88. Found: C, 79.91; H, 7.75.

Summary

1. The Friedel–Crafts reaction, involving the nuclear introduction of alkyl and acyl groups, has been effected with a miscellany of furan compounds.

2. The same reaction has been shown to take place with some negatively substituted benzenoid types having pronounced aromatic characteristics.

3. The preferential and exclusive substitution in the furan nucleus of a symmetrical ketone like 2-furyl phenyl ketone, and the alkylation and acylation of ethyl furoate but not of ethyl benzoate, together with the fact that benzene can be used as a medium for some Friedel–Crafts reactions of furan are advanced as additional supporting evidence for the concept that furan has super-aromatic properties.

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Melting Point Curves of Some Alkyl and Acetylenic Mercury Derivatives

By Thomas H. Vaughn with R. J. Spahr and J. A. Nieuwland

In recent communications the preparation and properties of a number of compounds belonging to the series of normal dialkynylmercurys[1] and normal bisalkylmercury acetylides[2] have been reported. When the melting points of the members of these series were plotted against the number of carbons in the alkyl group it was noticed that there appeared to be an almost constant difference of approximately 30° between the two curves.

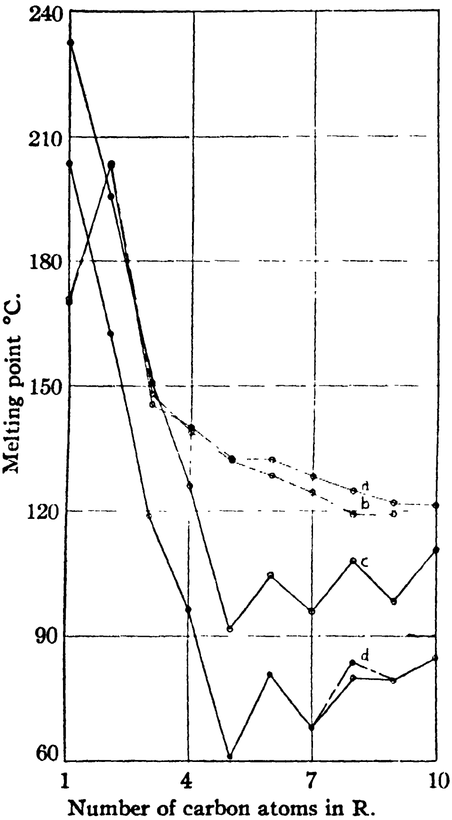

Fig. 1.—Melting point curves. Curves a and b have been elevated 10° in order to minimize overlapping.

That such a constant difference existed seemed rather unusual and interesting particularly in view of the character of the central groups. In order to have more complete data for comparison we have completed the bisalkylmercury acetylide series up to the decyl member. The melting point curves for both series as high as the decyl derivative are shown in Fig. 1. Although the difference is not constant the curves show a remarkable similarity.

In the reported preparation of the lower members of this series[2] the corresponding alkyl mercury halide was dissolved in 10% aqueous potassium hydroxide and the solution treated with acetylene. With the higher members it was not practical to use aqueous solutions or even 10% alcoholic potassium hydroxide because of the low solubility of the substituted mercury halides. Accordingly very dilute alcoholic solutions of caustic were used, care being taken, however, that an excess of the amount of potassium hydroxide necessary to convert the

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(1) Vaughn, This Journal, 55, 3453 (1933).

(2) Spahr, Vogt and Nieuwland, *ibid.*, 55, 2465 (1933).

alkyl mercury halide to the hydroxide was present.[3] The yields from the modified procedure are uniformly high.

Since the use of a common medium for crystallization would considerably enhance the value of these derivatives in identifying alkyl mercury halides,[2] *n*-propanol was tried on a number of bisalkylmercury acetylides and was satisfactory for the methyl, ethyl, propyl, hexyl, heptyl, octyl, nonyl, decyl, phenyl and *p*-tolyl derivatives.

Heptyl, octyl[4] and nonyl[5] mercury bromides were prepared for use in this work and it was found that after repeated crystallizations from alcohol melting point values 3 to 6° higher than those reported in the literature were obtained. The melting point data in the literature for the entire series were then plotted against molecular weights (Curve b, Fig. 1).[6] It was found that the regular alternation usually found in such curves was absent. The entire series as high as decyl was then prepared and purified in these laboratories and the melting point data obtained are tabulated in Table I along with the data from the literature.

TABLE I

ALKYL MERCURY BROMIDES

Alkyl mercury bromide	Crystn.	M. p. in literature, °C.	M. p. observed, °C.
Methyl	2	160[a]	160.8–161.3
Ethyl	6	193.5[b]	193.0
Propyl	4	138[b]	135.4
Butyl	4	129[c]	129.9–130.0
Amyl	3	122[b]	122.2–122.4
Hexyl	2	118.5[b]	122.0–122.2
Heptyl	3	114.5[b]	117.8–118.4
Octyl	3	109[b]	114.8–115.0
Nonyl	4	109[d]	111.6–112.0
Decyl	3	...	111.0–111.4

[a] Crymble, *J. Chem. Soc.*, **105**, 668 (1914).

[b] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[c] Marvel and Gould, *ibid.*, **44**, 153 (1922).

[d] Hill, *ibid.*, **50**, 167 (1928).

When these new values are plotted (Curve a,[6] Fig. 1) a small but regular alternation is apparent.

The melting point and analytical data for the new bisalkylmercury acetylides are tabulated in Table II.

Experimental Part

Alkyl Alcohols.—Hexanol, heptanol, octanol, nonanol and decanol were obtained by the action of ethylene oxide on the proper Grignard reagent. The procedure em-

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[3] Spahr, Vogt and Nieuwland, THIS JOURNAL, **55**, 3728 (1933).

[4] Marvel, Gauerke and Hill, *ibid.*, **47**, 3009 (1925).

[5] Hill, *ibid.*, **50**, 167 (1928).

[6] In plotting this curve and Curve a, 10° was added to the actual melting point values in order to minimize overlapping.

TABLE II

BISALKYLMERCURY ACETYLIDES

Acetylide	Formula	M. p., °C.	Hg analyses, % Calcd.	Hg analyses, % Found
Bisheptylmercury	$C_7H_{15}Hg—C\equiv C—HgC_7H_{15}$	95.8- 96.0	64.37	64.05
Bisoctylmercury	$C_8H_{17}Hg—C\equiv C—HgC_8H_{17}$	108.0	61.58	61.35
Bisnonylmercury	$C_9H_{19}Hg—C\equiv C—HgC_9H_{19}$	98.0- 98.8	59.04	59.31
Bisdecylmercury	$C_{10}H_{21}Hg—C\equiv C—HgC_{10}H_{21}$	110.4-111.0	56.70	56.51

ployed was based on that of Dreger[7] but was modified in the manner of adding the ethylene oxide and in the method of working up the reaction products. These two modifications shorten the time of preparation by approximately eight to ten hours.

Preparation of Octanol.—A solution of 330 g. of hexyl bromide in 700 ml. of ether was added in the usual manner to 48 g. of magnesium turnings contained in a 2-liter 3-necked flask fitted with dropping funnel, mercury-sealed Bennings stirrer[8] and reflux condenser. As soon as the reaction was completed (thirty to forty-five minutes) the flask was placed in an ice-salt bath and the reflux condenser replaced by a liquid ammonia cooled spiral condenser.[9] The dropping funnel was replaced by an inlet tube reaching almost to the surface of the liquid and 95 g. of ethylene oxide added as rapidly (forty-five to sixty minutes) as the vigorous refluxing permitted. The cooling bath was removed and after refluxing ceased 250 to 275 ml. of ether was removed by distillation from a water-bath. Three hundred and thirty milliliters of dry benzene was added and the distillation continued without interruption of stirring until the temperature of the effluent vapor reached 65°. The mixture was then refluxed for one hour and hydrolyzed with ice cold 10% sulfuric acid. The benzene layer was separated and washed twice with 10% sodium hydroxide solution. The benzene was removed by distillation and the residue fractionated under reduced pressure. The yield was 185 g. (71% of the theoretical) of material boiling at 105° at 15 mm. The same procedure was followed in preparing other alcohols. The following yields were obtained: hexanol, 59%; heptanol, 58%; nonanol, 55%; decanol, 52%.

Alkyl Bromides.—The bromides were prepared by the action of phosphorus tribromide on the corresponding alcohols. Yields of 60 to 80% were obtained.

Alkyl Mercury Bromides.—These compounds were prepared in tenth molar quantities by the action of an excess of mercuric bromide on the corresponding alkylmagnesium bromide.[4] In the preparation of methyl mercury bromide the methyl bromide was prepared by dropping phosphorus tribromide into methyl alcohol. The gas was led through a water-cooled reflux condenser and sprayed through concentrated sulfuric acid to remove alcohol. After passing over soda lime the gas was led directly into the reaction flask which was equipped with a liquid ammonia cooled spiral reflux condenser.[9] The reaction was easily controlled by regulating the dropping of the phosphorus tribromide.

The alkyl mercury bromides were purified by recrystallizations from alcohol until no further change in the melting point was observed. The number of crystallizations required by the several bromides is given in Table I. All melting points were taken by the capillary tube method in a bath whose temperature was rising 1.5° per minute at the fusion point, using standardized partial immersion thermometers graduated in tenths of a degree.

Alkyl Mercury Acetylides.—These were prepared by a modification of the method of Spahr, Vogt and Nieuwland.[2]

Bis Decylmercury Acetylide.—Two grams of decyl mercury bromide and 2 g. of potassium hydroxide were dissolved in 250 ml. of alcohol at room temperature. The

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(7) Dreger, "Organic Syntheses," Coll. Vol. I, 1932, pp. 299–301.

(8) Bennings, *Proc. Ind. Acad. Sci.*, **37**, 263 (1927).

(9) Vaughn and Pozzi, *J. Chem. Educ.*, **8**, 2433 (1931).

solution was filtered and treated with dry acetylene under a pressure of 10 cm. of mercury.[10] The precipitate of acetylide was collected on a fluted filter and after washing three times with 10 ml. of alcohol crystallized twice from *n*-propanol. The filtrate from the reaction mixture on standing lost acetylene and, due to the decomposition of the monoalkylmercuri acetylide, deposited more of the bis compound.

Analysis of Compounds.—Decyl mercury bromide was analyzed according to the method of White.[11] Calcd. for $C_{10}H_{21}HgBr$: Hg, 47.56. Found: Hg, 47.40. The acetylides were decomposed by White's process[11] and the mercury determined by the volumetric procedure of Rupp.[12] Results are listed in Table I.

Summary

1. Decyl mercury bromide and four new bisalkylmercury acetylides have been prepared and their melting points reported.

2. *n*-Propanol has been found to be a suitable medium from which to crystallize members of the bisalkylmercury acetylide series.

3. The melting point curves of the dialkynyl mercurys and the bisalkylmercury acetylides are very similar and lie approximately 29° apart.

4. The values for the melting points of the alkyl mercury bromides as high as the decyl member have been determined on pure samples. The melting point curve shows a small but regular alternation.

5. A simplified procedure for the preparation of straight chain alcohols has been reported.

[10] Vaughn, *ibid.*, **9**, 528 (1932).

[11] White, THIS JOURNAL, **42**, 2359 (1920).

[12] Rupp, *Chem.-Ztg.*, **32**, 1077 (1908).

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Preparation of *tert*-Butylacetic Acid and its Derivatives

BY AUGUST H. HOMEYER[1] WITH FRANK C. WHITMORE AND V. H. WALLINGFORD

This study was undertaken because of our interest in compounds containing the neopentyl group.[2]

No significant information is available on the preparation, properties or derivatives of *tert*-butylacetic acid. Although it has been reported[3] several times, its formation resulted from reactions unsuited for its preparation in quantity and high purity, and only two derivatives[4] have been prepared from it. Difficulty in its synthesis arises from the failure[5] of *tert*-butyl halides to react satisfactorily with the sodium derivatives of malonic or acetoacetic esters and the non-availability and non-reactivity of neopentyl halides.[6]

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[1] Mallinckrodt Research Fellow.

[2] Whitmore and co-workers, THIS JOURNAL, 1932–1933.

[3] (a) Delacre [*Bull. sci. acad. roy. Belg.*, 7–41 (1906); *Chem. Zentr.*, I, 1233 (1906); *J. Chem. Soc.*, **90** [I], 476 (1906)] by oxidation of 3,3-dimethylbutanol-1; (b) Ozanne and Marvel [THIS JOURNAL, **52**, 5270 (1930)], by ozonolysis of 2-bromo-4,4-dimethylpentene-1; (c) McCubbin and Adkins, [*ibid.*, **52**, 2549 (1930)] by oxidation of 4,4-dimethylpentanone-2. (d) McCubbin [*ibid.*, **53**, 357 (1931)] by oxidation of dineopentyl ketone. (e) Whitmore and Church, [*ibid.*, **54**, 3710 (1932)] by ozonolysis of 2,4,4-trimethylpentene-1; (f) Favorsky and Opel [*J. Russ. Phys.-Chem. Soc.*, **50**, 34–80 (1918); *Chem. Abstracts*, **18**, 2498 (1924)] by oxidation of *tert*-butylallene; (g) Favorsky and Morew [*J. Russ. Phys.-Chem. Soc.*, **50**, 571–581 (1918); *Chem. Abstracts*, **18**, 2496 (1924); *Chem. Zentr.*, III, 998 (1923)] by oxidation of *tert*-butylacetylene.

tert-Butylacetic acid is readily prepared in 80–90% yield by degradation of 4,4-dimethylpentanone-2 with sodium hypobromite. Since the ketone may enolize in two ways, it is surprising that halogenation is limited to the methyl group.[7] This fact suggests that the hydrogen atoms of the neopentyl group are closely held.

Although *tert*-butylacetic acid contains a neopentyl group it shows no abnormalities in its reactions. Ethyl *tert*-butylacetate yields the amide by ammonolysis in contrast to ethyl trimethylacetate[8] which does not undergo this reaction. The Hofmann rearrangement[9] of *tert*-butylacetamide gives neopentylamine. Neopentyl cyanide is obtained from the amide by action of phosphorus oxychloride.

Since the bromination of acids and acyl halides takes place through enolization[10] followed by addition, no rearrangement would be expected to occur. The bromination of *tert*-butylacetic acid and its acid chloride yields the corresponding α-bromo compounds. No rearranged products were found. α-Bromo-*tert*-butylacetic acid has been reported as having been prepared from a compound believed to be α-bromo-*tert*-butylmalonic acid.[11] The product melted at 57° whereas α-bromo-*tert*-butylacetic acid prepared by the present method melts at 72–73°. Attempts by Richard[12] to prepare α-halogenated acids from α-hydroxy-*tert*-butylacetic acid and its esters by the action of phosphorus halides failed, probably due to the formation of stable esters of phosphorus acids.

The replacement of the bromine of α-bromo-*tert*-butylacetamide by hydrogen through the action of zinc and acetic acid gave *tert*-butylacetamide quantitatively.[13]

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(4) The *p*-bromophenacyl ester, m. p. 81–81.5°; Ref. 3b. The amide, m. p. 132°; Refs. 3c, d, e.

(5) Unpublished work of W. R. Trent of this Laboratory. Also, *tert*-butylmagnesium chloride does not react satisfactorily with ethylene oxide to give 3,3-dimethylbutanol-1, which might be oxidized to the corresponding acid. Abderhalden and Rossner obtained some *tert*-butylmalonic ester by the reaction of *tert*-butyl bromide with sodiomalonic ester at room temperature, *Z. physiol. Chem.*, **163**, 177 (1927).

(6) Whitmore and Fleming, THIS JOURNAL, **54**, 3460 (1932); **55**, 4161 (1933).

(7) *Cf.* Hurd and Thomas, *ibid.*, **55**, 1646 (1933).

(8) The statement made by Bannow in a note to a paper by E. Fischer and Dilthey [*Ber.*, **35**, 856 (1902)] that ethyl trimethylacetate does not yield the amide when heated with alcoholic ammonia has been confirmed in this Laboratory.

(9) Whitmore and Homeyer, THIS JOURNAL, **54**, 3435 (1932).

(10) Watson, *Chem. Rev.*, **7**, 173–201 (1930).

(11) Abderhalden and Rossner, *Z. physiol. Chem.*, **163**, 177 (1927).

(12) Richard, *Ann. chim. phys.*, [8] **21**, 402 (1910).

(13) *Cf.* Bougault [*ibid.*, [9] **5**, 341 (1916)] who prepared α,α-dibromo-*tert*-butylacetamide by an indirect method and reduced it to *tert*-butylacetamide with zinc and acetic acid.

Experimental

4,4-Dimethylpentanone-2.—This material was prepared by W. R. Trent from diisobutylene by oxidation with sodium dichromate and sulfuric acid;[14] b. p. 124–125° (733 mm.); n_D^{20} 1.4028.

***tert*-Butylacetic Acid.**—One kg. of finely crushed ice and a solution of 525 g. of sodium hydroxide in 2 liters of ice water were placed in a 5-liter 3-necked flask fitted with a mercury-sealed stirrer, thermometer and dropping funnel. The flask was cooled in a large bath of ice and salt water. Two hundred forty cc. of bromine (4.75 moles) was added from the dropping funnel during one hour to the stirred sodium hydroxide solution. As soon as the sodium hypobromite solution had been prepared, 171 g. of 4,4-dimethylpentanone-2 was added during about ten minutes. The solution was stirred for fourteen hours; then the mixture was steam distilled. Stirring was continued during distillation to prevent bumping. The distillate amounted to about 600 cc. of water and 175 g. of a mixture of bromoform and carbon tetrabromide. The residue from the steam distillation was acidified by addition of 600 cc. of concentrated sulfuric acid (excess) from the dropping funnel, the delivery tube of which dipped below the surface of the stirred liquid. The *tert*-butylacetic acid was steam distilled; the distillate amounted to about 1100 cc. The oil layer was separated (weight 151 g.) and the aqueous layer was extracted with 200 cc. of ether. After evaporating the ether the extracted material amounted to 17 g. and was added to the main portion. The product was dried and purified by distillation at reduced pressure through a 70 × 1 cm. indented column of the total condensation, adjustable take-off type.[15] The yield was 155 g. of *tert*-butylacetic acid or 89% of the theoretical. Its properties[16] are: b. p. 96° (26 mm.); 183.0–183.3° (739 mm.) (Cottrell); m. p. 6–7°; n_D^{20} 1.4096; d_4^{20} 0.9124; M.R. found (Lorentz–Lorenz formula): 31.48; calcd. (Eisenlohr values): 31.46.

The sodium salt crystallized in plates from alcohol on dilution with ether. *Anal.* Calcd. for $C_6H_{11}O_2Na$: Na, 16.65. Found: Na, 16.59.

The calcium salt is not very soluble in either hot or cold water. *Anal.* Calcd. for $C_{12}H_{22}O_4Ca$: Ca, 14.82. Found: Ca, 14.81.

***tert*-Butylacetyl chloride** was prepared by means of thionyl chloride in 93% yield; b. p. 79–81° (150 mm.); n_D^{20} 1.422; d_4^{20} 0.968; M.R. found: 35.2, calcd. 34.8.

***tert*-Butylacetamide** was obtained in 82% yield from the acid chloride and aqueous ammonia below 10°. *tert*-Butylacetamide crystallized in large colorless plates on the addition of petroleum ether to its solution in ethyl acetate, m. p. 132°.

Five cc. of ethyl *tert*-butylacetate sealed in a tube with 20 cc. of absolute alcohol saturated with ammonia at 0° yielded no amide after standing at room temperature for five months. Four grams of the original ester separated from the ammoniacal solution when it was diluted with water. Five cc. of ethyl *tert*-butylacetate sealed in a tube with 10 cc. of concentrated aqueous ammonia showed no signs of reaction after standing at room temperature for four months. Heating at 100° for twenty-three hours caused no change but after heating at 150–170° for ten days the ester layer had disappeared completely and 1.1 g. of *tert*-butylacetamide, m. p. 131–131.5°, and about 2 cc. of *tert*-butylacetic acid were isolated.

A tube containing 5 cc. of ethyl trimethylacetate and 20 cc. of absolute alcohol saturated with ammonia at 0° was kept at room temperature for five months and then

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(14) See Butlerow, *Ann.*, **189**, 46–83 (1877). Some of the earlier batches of ketone were made by ozonolysis of 2,4,4-trimethylpentene-1; *cf.* Ref. 3e.

(15) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(16) The boiling points given in the literature (Ref. 3) for *tert*-butylacetic acid vary from 175 to 190° and the freezing point according to Delacre (Ref. 3a) is −11°. The values given in "International Critical Tables," Vol. I, p. 203, b. p. 190°, m. p. −11°, appear to be based on Delacre's work.

was heated at 100° for seventeen hours. The product yielded 4 g. of the original ester but no amide was detected. In a similar experiment the tube was heated at 190° for sixty hours. A crystalline mass was obtained which disappeared completely when 10 cc. of water was added. Further dilution gave 3 g. of the original ester but no amide could be isolated. In a third experiment with ethyl trimethylacetate and methyl alcoholic ammonia the tube was heated at 200° for twenty-four hours. The crystalline mass was filtered off before adding water. It quickly evaporated from the suction filter. No amide could be detected.

tert-**Butylacetdiethylamide** was obtained in 79% yield as a viscous oil, b. p. 69° (3 mm.); n^{20}_D 1.4438.

tert-**Butylacetanilide** separated from ethyl acetate and petroleum ether as yellow crystals, m. p. 130°. It was decolorized by boiling its alcoholic solution with bone char and crystallized on diluting with water in small needles, m. p. 131°. *tert*-Butylacetanilide did not darken after keeping for six months. When mixed with *tert*-butylacetamide, m. p. 132°, the melting point was depressed to 100–105°.

tert-**Butylacetonitrile.**—Fifty-eight grams of *tert*-butylacetamide was made into a paste with 100 cc. of dry benzene and warmed on the steam-bath for twelve hours with 45 g. of phosphorus oxychloride. The liquid was decanted from the sludge, washed with water, with sodium bicarbonate solution and again with water and fractionated through a 30 × 1 cm. indented column. The yield of neopentyl cyanide was 44 g. or 90%; b. p. 135–136.4° (737 mm.); m. p. 32.5°.

Esters of *tert*-Butylacetic Acid.—*tert*-Butylacetyl chloride was added slowly to the pure alcohols. After warming on the steam-bath for a short time the product was washed with water, sodium bicarbonate solution, dried and fractionated. The yields were practically quantitative.

PROPERTIES OF *tert*-BUTYLACETATES

	B. p., °C. (mm.)	n^{20}_D	d^{20}_4	MR (obs.)	MR (calcd.)
Methyl	126.5 (739)[a]	1.3981	0.8710	36.06	36.06
Ethyl	144.5–144.7 (739)	1.4010	.8604	40.70	40.68
n-Propyl	92 (65)	1.4067	.8585	45.32	45.30
n-Butyl	91 (30)	1.4118	.8568	49.97	49.92
Benzyl[b]	146–148 (26)	1.4842			
Bornyl[b]	115–117 (5)	1.4615			
Menthyl[b]	114–115 (4–4.5)	1.4500			

[a] Cottrell b. p. [b] The yield of the last three esters was only 72–76%.

Vinyl Diacetonealkamine *tert*-Butylacetate Hydrochloride.—Nine grams of *tert*-butylacetyl chloride and 8.5 g. of vinyl diacetonealkamine hydrochloride were heated together at 100° for two hours, at 140° for two hours more and finally at 150–160° for three hours. Hydrogen chloride was evolved and the mixture became fluid. The product was dissolved in 40 cc. of water. After making strongly alkaline with sodium hydroxide the free ester was extracted with ether, dried over potassium carbonate and the hydrochloride was precipitated by saturating the solution with hydrogen chloride. Nine grams of vinyl diacetonealkamine *tert*-butylacetate hydrochloride was obtained as a white crystalline powder, m. p. *ca.* 210° with decomposition.

α-Bromo-*tert*-Butylacetic Acid.—Forty-five grams of dry *tert*-butylacetic acid, 24 cc. of dry bromine and 2 cc. phosphorus trichloride in a flask connected to a reflux condenser were warmed at 60–70° for three hours and finally at 100° for one hour. The product solidified on cooling. It was distilled from a Claisen flask, an ordinary distilling flask cooled by a stream of water being used as a receiver in which the product solidified. The fraction distilling at 102–109° (2 mm.) weighed 61 g., 81%; m. p. 72–73°.

Anal. Calcd. for $C_6H_{11}O_2Br$: Br, 40.98. Found: Br, 40.34.

Attempts to isolate salts of this acid failed.

α-Bromo-*tert*-butylacetyl Bromide.—Thirty-five grams of dry *tert*-butylacetic acid and 3.9 g. of red phosphorus were treated in a flask fitted with a reflux condenser with 35 cc. of dry bromine added dropwise. The mixture was shaken at frequent intervals. After adding all the bromine the reaction mixture was warmed on the steam-bath for one and one-half hours. The crude product was decanted into a Claisen flask and distilled. The bromide was obtained as a fuming liquid, b. p. 82° (18 mm.).

α-Bromo-*tert*-butylacetamide.—Thirty grams of the bromo acid bromide was added dropwise to 75 cc. of concentrated aqueous ammonia cooled in ice and stirred. The amide was filtered off and recrystallized from ethyl acetate. α-Bromo-*tert*-butylacetamide, m. p. 138°; yield 16 g. or 71%.

Anal. Calcd. for $C_6H_{12}OBrN$: Br, 41.19. Found: Br, 40.87.

Five grams of the bromoamide was dissolved in a solution of 15 cc. of acetic acid and 7 cc. of water. Four grams of 30-mesh zinc was added and the mixture was warmed on the steam-bath for two hours. Thirty cc. of warm water was added to dissolve the amide and the solution was filtered. The amide was extracted with two 40-cc. portions of ether. Evaporation yielded 2.9 g. of *tert*-butylacetamide (97% yield) which melted at 129° before recrystallization. After crystallizing from ethyl acetate by diluting with petroleum ether it melted at 131° and showed no depression when mixed with a known sample of *tert*-butylacetamide.

α-Bromo-*tert*-butylacetdiethylamide was prepared in 72% yield from the bromide; b. p. 106–109° (5 mm.); m. p. 35–37°.

Anal. Calcd. for $C_{10}H_{20}OBr_2N$: Br, 31.96. Found: Br, 31.34.

α-Bromo-*tert*-butylacetyl chloride was prepared in 92% yield from *tert*-butylacetyl chloride; b. p. 93–97° (37 mm.). The amide prepared from this product was identical with that obtained from the bromo-acid bromide.

α-Bromo-*tert*-butylacetyl Urea.—Ten grams of urea crystals and 13 g. of α-bromo-*tert*-butylacetyl chloride were mixed and warmed on the steam-bath for a few minutes. After keeping at room temperature for twenty-four hours, the reaction mixture was warmed to 100° for one hour. The product was washed with water and dilute sodium bicarbonate solution, and the residue was recrystallized from ethyl acetate. α-Bromo-*tert*-butylacetyl urea melts at 188.5°; yield 10 g. or 70%.

Anal. Calcd. for $C_7H_{13}O_2BrN_2$: Br, 33.72. Found: Br, 33.70.

Ethyl α-bromo-*tert*-butylacetate was obtained in 75% yield from α-bromo-*tert*-butylacetyl chloride; b. p. 93° (23 mm.); n^{20}_D 1.4510.

Anal. Calcd. for $C_8H_{15}O_2Br$: Br, 35.83. Found: Br, 36.43.

Menthyl α-Bromo-*tert*-butylacetate.—Twenty-three grams of α-bromo-*tert*-butylacetyl chloride was added to 17 g. of Mallinckrodt menthol, U. S. P. After warming on the steam-bath it was washed and distilled from a Claisen flask at reduced pressure, b. p. 148–150° (4 mm.); n^{20}_D 1.4753.

Anal. Calcd. for $C_{16}H_{29}O_2Br$: Br, 23.99; found, 25.48.

Bornyl α-bromo-*tert*-butylacetate; b. p. 148–153° (4–5 mm.); n^{20}_D 1.4876.

Benzyl α-bromo-*tert*-butylacetate; b. p. 145–147°(4.5 mm.); n^{20}_D 1.5160. Some benzyl chloride was also formed.

Summary

tert-Butylacetic acid has been prepared in good yield and high purity from 4,4-dimethylpentanone-2 and sodium hypobromite. Many of its

derivatives have been prepared and characterized. Bromination of the acid or its chloride yielded the corresponding α-bromo compounds. Several derivatives of α-bromo-*tert*-butylacetic acid have been prepared. No rearranged products were observed.

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The Chloro Derivatives of *m*-Cresol

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This study had as its objective a survey of those chloro derivatives of *m*-cresol in which the chlorine atoms are ortho or para to the hydroxyl group. Information concerning these compounds is meager and often contradictory.

2-Chloro-*m*-cresol.—Gibson[2] describes 2-chloro-*m*-cresol, prepared from its methyl ether, as massive, ill-defined, transparent crystals melting at 55–56°. When prepared from 2-nitro-*m*-cresol or from *m*-cresol by chlorination of the disulfonic acid, it formed clusters of fragile tetragonal crystals which melted at 49–50°.

The 2-nitro-*m*-cresol was prepared from *m*-cresol by nitration in fuming sulfuric acid[3] and reduced to the corresponding amino compound by means of sodium hydrosulfite. Forty-four grams of 2-amino-*m*-cresol yielded, upon diazotization and treatment with cuprous chloride (using the technique developed by Marvel and McElvain for the preparation of *o*- and *p*-chlorotoluene[4]), 32 g. of 2-chloro-*m*-cresol boiling at 198–199°.

Anal. Calcd. for C_7H_7OCl: Cl, 24.91. Found: Cl, 24.77.

The clorination of *m*-cresol in fuming sulfuric acid was effected by a method similar to the one used for the preparation of 2-nitro-*m*-cresol[3] except that, in the place of nitric acid, one mole equivalent of chlorine[5] was passed into the acid solution. Chlorine was not readily absorbed. After hydrolysis at 200°, the resulting oil which separated from the distillate was fractionated five times. It gave a small fraction boiling at 198–199° and a larger fraction at 199–205° which consisted mostly of the unreacted *m*-cresol. The 198–199° fraction was set in the ice box and seeded with 2-chloro-*m*-cresol prepared from 2-nitro-*m*-cresol. The crystals that separated out from the oil were suction filtered and recrystallized from petroleum ether.

Chlorination of the disulfonic acid of *m*-cresol (prepared by sulfonation with concd. sulfuric acid) in the presence of five moles of sodium hydroxide and subsequent hydrolysis in acid solution at 200° gave 2-chloro-*m*-cresol and a fraction boiling at 235–245° which consisted of 2,6-dichloro-*m*-cresol to be described later.

4-Chloro-*m*-cresol.—The preparation of 4-chloro-*m*-cresol from *m*-cresol by direct chlorination in the vapor state,[6] or in solution,[2,7] or by

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(1) Presented in partial fulfilment of the requirements for the Ph.D. degree.

(2) Gibson, *J. Chem. Soc.*, 1424–1428 (1926).

(3) Hodgson and Beard, *J. Chem. Soc.*, **127**, 498 (1925).

(4) "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 33.

(5) Houben, "Die Methoden der organischen Chemie," Vol. III, p. 799.

(6) Biedermann, *Ber.*, **6**, 325 (1873).

(7) Kalle and Co., German Patents 90,847, 93,694.

treatment of the cresol with sulfuryl chlorine[8,9,10] or a mixture[11] of sulfuryl chloride and chlorine is described in the literature. The melting point is given as 56, 66, 52 and 57°; the boiling point as 240, 231 and 234°. The proof of structure was effected by Gibson[2] by oxidation of the methyl ether prepared from 4-chloro-*m*-cresol which he obtained by fractioning a mixture of the three monochloro-*m*-cresols obtained by chlorination in carbon tetrachloride.

We have prepared pure 4-chloro-*m*-cresol by the following sequence.

Carefully purified *o*-chlorotoluene was nitrated according to Goldschmidt and Hönig[12] and the nitro compound was reduced with tin and hydrochloric acid. After heating for half an hour to complete the reduction, the mixture was cooled, made alkaline with sodium hydroxide and steam distilled. The amine which solidified in the distillate was recrystallized from ligroin; m. p. 83.5°.[13] Eleven grams of the 3-amino-6-chlorotoluene was treated with hydrochloric acid and diazotized in the usual manner. The diazotized solution was heated on a steam-bath for half an hour, during which time a dark oil separated on top of the liquid. After steam distillation, the distillate was salted out and extracted with ether. Five and one-half grams of 4-chloro-*m*-cresol distilled over at 231–233°. It crystallized in clusters of very fine needles melting at 55.5°.

Anal. Calcd. for C_7H_7OCl: Cl, 24.91. Found: Cl, 24.74.

6-Chloro-*m*-cresol.—Raschig[9] obtained this compound together with 4-chloro-*m*-cresol by chlorination of *m*-cresol with sulfuryl chloride. He was unable to isolate it in solid form and described it as colorless liquid with a camphor-like odor which boiled at 197°. It was prepared by Hodgson and Moore[14] from 4-chloro-*m*-nitrotoluene by reduction, diazotization and hydrolysis. They give the melting point of 45°. Its formation by the diazotization and hydrolysis of 3-amino-4-chlorotoluene is also described by Kraay[15] as a check on its preparation from 3,4-dichlorotoluene by treatment with sodium methoxide (m. p. 46°). Gibson[2] who isolated 6-chloro-*m*-cresol from the products of direct chlorination of *m*-cresol gave 46° as the melting point.

We have repeated the preparation of 6-chloro-*m*-cresol from 4-chloro-*m*-nitrotoluene[14] after preparing the latter from both *p*-toluidine[16] and from *p*-chlorotoluene.[12] As a further check it was prepared from 6-nitro-*m*-cresol[17] by reduction according to the method of Raiford,[18] diazotization and treatment with cuprous chloride[4] (31 g. of 6-nitro-*m*-cresol gave 10.5 of 6-chloro-*m*-cresol). In all cases the product boiled at 197–198° and crystallized in rhombohedra melting at 46°.

Anal. Calcd. for C_7H_7OCl: Cl, 24.91. Found: Cl, 24.69.

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[8] Peratoner and Condorelli, *Gazz. chim. ital.*, **28**, I, 213 (1898).

[9] Raschig, German Patent 232,071.

[10] Liebrecht, German Patent 233,118.

[11] Laschinger, U. S. Patent 1,847,566.

[12] Goldschmidt and Hönig, *Ber.*, **19**, 2440 (1886).

[13] Bamberger, *ibid.*, **35**, 3701 (1902).

[14] Hodgson and Moore, *J. Chem. Soc.*, 2036 (1926).

[15] Kraay, *Rec. trav. chim.*, **49**, 1082–1092 (1930).

[16] Gattermann and Kaizer, *Ber.*, **18**, 2600 (1885).

[17] Staedel and Kolb, *Ann.*, **259**, 210 (1890).

[18] Raiford, *Am. Chem. J.*, **46**, 419 (1911).

Monochloro-*m*-cresols by Direct Chlorination.—One mole of *m*-cresol chlorinated in 400 cc. of chloroform at 0° with one mole of chlorine[8] gave after six distillations 33 g. boiling at 196–199°; 20 g. at 199–230°; and 70 g. at 230–238°. The 199–230° fraction consisted mostly of the unreacted *m*-cresol. The 230–238° fraction gave upon purification 32 g. of 4-chloro-*m*-cresol. The 196–199° fraction gave upon further distillation 18.5 g. boiling at 197–198°. When cooled to −10° and seeded with 6-chloro-*m*-cresol prepared from 6-nitro-*m*-cresol, it partially solidified. The crystals were filtered at once by suction. The purified product melted at 46°. The oil that remained after the complete removal of 6-chloro-*m*-cresol yielded 2-chloro-*m*-cresol when chilled and seeded.

4,6-Dichloro-*m*-cresol.—The melting point of 4,6-dichloro-*m*-cresol is given by v. Walther and Zipper[19] as 45–46° and by Tanaka and Morikawa[20] as 58°. We obtained by the following sequences fine flat needles melting at 71.5–72.5° and boiling at 235–236°.

(*a*) Chlorination of 6-nitro-*m*-cresol in cold chloroform or acetic acid solution with two moles of chlorine gave only the 4-chloro-6-nitro-*m*-cresol (m. p. 131–133°).[21] This was reduced with stannous chloride and hydrochloric acid.[18] The resulting hydrochloride was diazotized and treated with a cold solution of cuprous chloride.[4] Upon steam distillation, 4,6-dichloro-*m*-cresol separated out from the distillate as an oil.

Anal. Calcd. for C_7H_7OCl: Cl, 40.11. Found: Cl, 40.39.

(*b*) Pure 4,6-dinitro-*m*-cresol was obtained from 4-nitro-*m*-cresol[17] by nitration in acetic acid solution according to Gibbs and Robertson.[22] After standing overnight, the reaction mixture was poured into water and the oil that separated out was purified by distillation under vacuum. The product was separated from unchanged 4-nitro-*m*-cresol by fractional crystallization from benzene. Further recrystallization from dilute acetic acid gave a product melting at 71°.[23] After reduction with stannous chloride and hydrochloric acid,[18] both amino groups were diazotized and replaced with chlorine by the Sandmeyer method.[4] This method gave a smaller yield of 4,6-dichloro-*m*-cresol than the preceding.

The direct chlorination of either 4-chloro-*m*-cresol or 6-chloro-*m*-cresol gave as one of the products 4,6-dichloro-*m*-cresol (see below).

It may be significant that the 4,6-dichloro-*m*-cresol described by v. Walther and Zipper[19] has a melting point identical with 2,4,6-trichloro-*m*-cresol,[19,26,27] while that described by Tanaka and Morikawa melted at the same temperature as 2,4-dichloro-*m*-cresol.

2,4-Dichloro-*m*-cresol.—Tanaka and Morikawa[20] and Datta and Mitter[24] report the melting point of 2,4-dichloro-*m*-cresol as 44 and 45°. The latter workers state that their compound is identical with the dichloro-*m*-cresol prepared by Claus and Schweitzer[25] who gave its melting point as 46°. As was pointed out by Crowther and McCombie[26] and also supported by the work of Raiford,[27] Claus and Schweitzer's dichloro compound was

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(19) V. Walther and Zipper, *J. prakt. Chem.*, [2] **91**, 374 (1864).

(20) Tanaka and Morikawa, *J. Chem. Soc. Japan*, **51**, 275–277 (1930).

(21) Kenner, Tod and Withan, *J. Chem. Soc.*, **127**, 2349 (1925); v. Walther and Zipper, *J. prakt. Chem.*, [2] **91**, 411 (1864).

(22) Gibbs and Robertson, *J. Chem. Soc.*, **105**, 1889 (1914).

(23) Will, *Ber.*, **47**, 712 (1914); Sane and Joshi, *J. Indian Chem. Soc.*, **5**, 299-301 (1928).

(24) Datta and Mitter, THIS JOURNAL, **41**, 2033 (1919).

(25) Claus and Schweitzer, *Ber.*, **19**, 930 (1886).

(26) Crowther and McCombie, *J. Chem. Soc.*, **103**, 545 (1913).

(27) Raiford, *Am. Chem. J.*, **46**, 424 (1911).

most probably the 2,4,6-trichloro-*m*-cresol of the same melting point. The same might be said of the 2,4-dichloro-*m*-cresol prepared by Tanaka and Datta and their co-workers.

Attention might be called to the fact that in Datta and Mitter's work of converting the disulfonic acid into the corresponding dichloro compound, chlorine was passed in to "saturation" and the resulting product was not analyzed. Furthermore, they state that 2,4-dichloro-*m*-cresol was the sole product of chlorinating *m*-cresol-*p*-sulfonic acid. It is hard to see why the second atom of chlorine should enter the 2-position more readily than the 6-position.

The 2,4-dichloro-*m*-cresol we prepared by careful chlorination of a cold chloroform solution of 2-chloro-*m*-cresol or 4-chloro-*m*-cresol boiled at 234° and melted at 58°.

Anal. Calcd. for C_7H_6OCl: Cl, 40.11. Found: Cl, 40.20.

2,6-Dichloro-*m*-cresol.—The literature gives no description of 2,6-dichloro-*m*-cresol.[25] When prepared by the following sequences it boiled at 240.5–242.5° and crystallized in prisms melting at 27°.

(*a*) Crude 4-nitro-*m*-cresol prepared by the method of Staedel and Kolb[17] was chlorinated with two moles of chlorine in glacial acetic acid. The crystals that separated out were filtered off and the filtrate poured into a large quantity of water from which another crop of crystals was obtained. Recrystallized from benzene both crops melted at 143° with decomposition.[28] The 2,6-dichloro-4-nitro-*m*-cresol was reduced with stannous chloride in the usual manner. (An attempt to liberate the amine from the hydrochloride by means of ammonium carbonate was not successful.) Eighty grams of hydrochloride was diazotized and the amino group replaced with hydrogen by means of an alkaline solution of stannous chloride;[29] yield 6 g.

Anal. Calcd. for $C_7H_6OCl_2$: Cl, 40.11. Found: Cl, 40.04.

(*b*) The fraction boiling at 235–245° obtained in the preparation of 2-chloro-*m*-cresol (p. 4214) was repeatedly fractionated. Most of it came over at 240–242.5°. This was shown by analysis, ester formation and chlorination to 2,4,6-trichloro-*m*-cresol to be 2,6-dichloro-*m*-cresol.

Dichloro-*m*-cresols by Direct Chlorination.—Chlorination of one mole of *m*-cresol in chloroform solution at 0° with two moles of chlorine gave a mixture which after five distillations gave 20 g. boiling at 233–235°; 82 g., at 235–237°; 27 g., at 237–240°; 13 g., at 240–250°. The crystals that separated out from the first three fractions upon standing were filtered at the pump and purified. A yield of 60 g. of pure 4,6-dichloro-*m*-cresol was obtained.

Crystals obtained from the mother liquor consisted of a mixture of both the 4,6- and 2,4-dichloro-*m*-cresols, the separation of which could be effected by dissolving in excess of petroleum ether and allowing to crystallize slowly in the ice box. Under these conditions the less soluble 2,4-dichloro-*m*-cresol was deposited around the edge of the beaker while the 4,6-isomer was deposited at the bottom.

More of the 2,4-dichloro compound was separated from the residual oil from which the crude 4,6-dichloro-*m*-cresol had been filtered, when this was allowed to stand for several days at −10°. The total yield of 2,4-dichloro-*m*-cresol was about 20 g. After all possible 2,4-dichloro-*m*-cresol had been chilled out, the residual oil from the first three fractions was combined with the fourth, which gave no crystals, and fractionated. A portion was collected at 240.5–242.5° which corresponds to the boiling point of 2,6-dichloro-*m*-cresol.

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[28] Raiford, THIS JOURNAL, **36**, 675 (1914).

[29] Houben, "Die Methoden der organischen Chemie," Leipzig, 1924, Vol. 4, p. 612.

Chlorination of Monochloro-*m*-cresols.—Upon chlorination in cold chloroform with one mole of chlorine: 2-chloro-*m*-cresol gave 2,4-dichloro-*m*-cresol and 2,6-dichloro-*m*-cresol; 4-chloro-*m*-cresol gave 2,4-dichloro-*m*-cresol and 4,6-dichloro-*m*-cresol; 6-chloro-*m*-cresol gave 4,6-dichloro-*m*-cresol and a small amount of oil which was doubtless the 2,6-isomer.

The 2,4- and 4,6-dichloro-*m*-cresols were isolated in the pure state. The 2,6-isomer was checked by formation of the *p*-toluene sulfonic ester and further chlorination to 2,4,6-trichloro-*m*-cresol.

Chlorination of the Dichloro-*m*-cresols.—All three dichloro-*m*-cresols gave almost the theoretical yields of 2,4,6-trichloro-*m*-cresol (m. p. 46°)[25] when chlorinated in chloroform with one mole of chlorine. This complete chlorination may be effected by chlorination of *m*-cresol itself in chloroform with three moles of chlorine

MELTING POINTS, ANALYSES AND CRYSTALLINE FORMS

	Benzoyl ester of *m*-cresol[30,31]	Benzene sulfonyl esters of *m*-cresol[30,31]	*p*-Toluene sulfonyl esters of *m*-cresol[30,31]
2-Chloro-*m*-cresol	Clusters of prisms	Prismatic plates	Fine lustrous prisms
4-Chloro-	Needle-like plates	Clusters of large needle-like plates	Clusters of needle-like plates
6-Chloro-	Prisms	Fine prisms	Prismatic plates
2,4-Dichloro-	Fine plates	Fine needle-like plates	Very shiny plates
2,6-Dichloro-	Clusters of small prismatic plates	Thin lustrous plates	Small prisms
4,6-Dichloro-	Mats of very fine needles	Clusters of elongated prisms	Very fine needles
2,4,6-Trichloro-	Very fine prismatic plates	Prismatic plates	Prismatic plates

		Chlorine, %			Chlorine, %			Chlorine, %	
	M. p., °C.	Calcd.	Found	M. p., °C.	Calcd.	Found	M. p., °C.	Calcd.	Found
2-Chloro-	55–56	14.38	14.47	58–58.5	12.74	12.11	96	12.13	11.75
4-Chloro-	86[2]	14.38	14.39	66	12.74	12.50	98	12.13[2]	12.69
6-Chloro-	38[2]	14.38	14.39	99	12.74	12.53	93–94[2]	12.13	11.92
2,4-Dichloro-	78–78.5	25.24	24.74	69.5	22.38	22.73	100–101	21.43	21.72
2,6-Dichloro-	90.5	25.24	25.57	70	22.38	22.82	92–92.5	21.43	21.21
4,6-Dichloro-	57.5	25.24	25.27	86	22.38	22.01	104–105	21.43	20.69
2,4,6-Trichloro-	53	33.73	34.00	121	30.28	30.21	92–93	29.12	29.24

The chloro-*m*-cresols described were purified by recrystallization from petroleum ether and their esters from ethyl alcohol. All cases of identity were established by the method of mixed melting points.

Summary

1. Chlorination of *m*-cresol in chloroform with one mole of chlorine gave 2-, 4- and 6-chloro-*m*-cresols.

2. Chlorination of *m*-cresol in chloroform with two moles of chlorine gave 2,4-, 2,6- and 4,6-dichloro-*m*-cresols.

3 The structures of the chloro-*m*-cresols were proved by a number of methods.

4. The benzoyl, benzene sulfonyl and *p*-toluene sulfonyl esters of all chloro-*m*-cresols were prepared.

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(30) Einhorn and Holland, *Ann.*, **301**, 95 (1898).

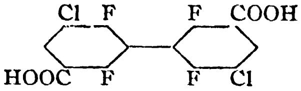
(31) Reverdin applied this method to sulfone chlorides (*Ber.* **35**, 1443 (1902).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

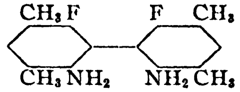
Stereochemistry of Diphenyls. XXXI.[1] Preparation and Properties of 2,2',6,6'-Tetrafluoro-3,3'-dicarboxy-5,5'-dichlorodiphenyl

BY E. C. KLEIDERER[2] AND ROGER ADAMS

In continuation of the investigation to determine the character of molecules containing atoms or groups of small volume in the 2,2',6,6' positions, the preparation of a tetrafluoro compound in this series has been undertaken. The specific substance finally obtained was 2,2',6,6'-tetrafluoro-3,3'-dicarboxy-5,5'-dichlorodiphenyl (I).



I



II

Under the conditions used it was found impossible to resolve this compound and no mutarotation of the salts was observed even at 0°. It would appear, then, that four fluorines are not sufficiently large to prevent free rotation of the phenyl groups.

A discussion of the structure of the 2,2'-difluoro-6,6'-diamino-3,3',5,5'-tetramethyldiphenyl (II) previously described by Kleiderer and Adams[3] has appeared in "Annual Reports of the Chemical Society of London.[4] Sidgwick has pointed out that if it is assumed that the hydrogen atoms of the amino groups in such a compound are turned out of the way, the inner spheres of the nitrogen and fluorine would not be expected to touch. He has presented a diagram drawn to scale illustrating this fact. He cites this as evidence that the repulsion of two groups extends beyond the range of the inner spheres and may be due to an envelope estimated at 0.5 Å. in thickness representing the large forces which cause the repelling of non-linked atoms.

Through the calculation previously made by Stanley and Adams[5] the prediction was made that a diaminodifluorodiphenyl should be capable of resolution but easily racemized. These facts were borne out by experiment. In this calculation it was assumed that the hydrogens on the nitrogens did play a role in the interference of the two groups. It seems dubious whether it is proper to assume, as Sidgwick has done, that hydrogens or particularly other atoms and groups attached to the atom combined with the ring will not exert steric influence. If rotation of the nitrogen attached to the carbon of the ring occurs,[6] the hydrogens on the nitrogen will be spinning in the circumference of a circle and should lead to a certain more or less constant, though perhaps small, residuum of interference extending beyond the inner sphere of the nitrogen atom. Moreover, the experimental evidence, though meager, is in favor of the assumption of an effect produced by atoms and groups on the atom attached to the ring. The restricted rotation in 2,5-di-(2,4-dimethylphenyl)-3,6-dibromohydroquinone[7] was not existent in the corresponding quinone. In the quinone molecule there is no hydrogen on the oxygen as is found in the hydroquinone. It must be admitted, however, that other factors may be involved in those molecules since the quinone and the hydroquinone nuclei are decidedly different in character. It has been shown that $-CONH_2$ restricts rotation to a greater extent than a COOH group.[8] An ethoxyl is more effective than a methoxyl in preventing free rotation of the rings.[9]

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[1] The previous paper in this series is, Searle and Adams, THIS JOURNAL, 55, 1649 (1933). See also Adams and Yuan, *Chem. Rev.*, 12, 261 (1933).

[2] Submitted as part of a thesis for the Degree of Doctor of Philosophy at the University of Illinois.

[3] Kleiderer and Adams, THIS JOURNAL, 53, 1575 (1931).

[4] Sidgwick, "Annual Reports Chem. Soc. of London," p. 69 (1932).

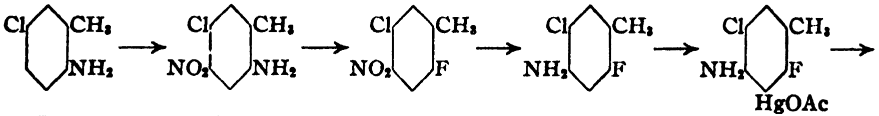
[5] Stanley and Adams, THIS JOURNAL, 52, 1200 (1930).

If a diagram is drawn for the tetrafluoro compound with the use of the same radii for fluorine and carbon as adopted by Sidgwick, it may be demonstrated that the two fluorines should not collide. Neither should they collide on the basis of calculations made by Stanley and Adams. On the other hand, if it is assumed that there is an envelope 0.5 Å. thick which may take part in the repulsion of the groups, resolution of the tetrafluoro compound might be expected. Since no resolution was obtained it may be concluded either that the effective envelope is much thinner than suggested by Sidgwick and that the inner spheres of two atoms must approach each other more closely in order to effect interference, or else that the hydrogens on a nitrogen or other atoms and groups attached to the atom combined to the ring contribute appreciably to the interference of 2,2′ substituents.

The 2,2′-difluoro-6,6′-dimethoxy compound described by Becker and Adams[10] was also non-resolvable but unfortunately as in the case of the hydrogens on the nitrogen there is no way to calculate the contribution of the methyl group to the interference of the methoxyl group. The conclusion that the methoxyl is less effective in interference than the amino group is warranted, since the corresponding amino derivative was resolvable.

Experimental

The preparation of the tetrafluoro compound (I) was made by the following series of reactions



III IV V VI VII

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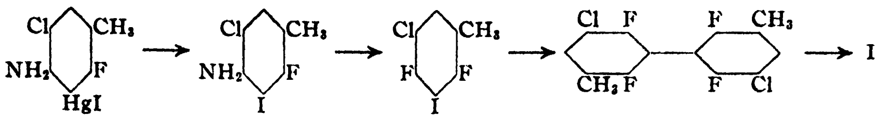
(6) Pauling, *Phys. Rev.*, **36**, 430 (1930); Hendricks, Posnjak and Kracek, This Journal, **54**, 2766 (1932).

(7) Browning and Adams, *ibid.*, **52**, 4098 (1930).

(8) Stanley, McMahon and Adams, *ibid.*, **55**, 706 (1933).

(9) Li and Adams, unpublished results.

(10) Becker and Adams, This Journal, **54**, 2973 (1932).



VIII IX X XI

The structure of the 2-amino-3-methyl-5-chloro-6-nitrobenzene (IV) was determined by converting it through 3-methyl-5-chloro-6-nitrobenzene to 3-methyl-5-chloro-6-aminobenzene, the acetate of which had the properties of this compound as made through another series of reactions. In a similar manner the position of the acetoxy-mercuri group in 1-acetoxy-mercuri-2-fluoro-3-methyl-5-chloro-6-aminobenzene (VII) was determined by replacing the acetoxymercuri group with bromine and then comparing the product with the bromine compound made by another procedure which would lead with reasonable certainty to a molecule of that structure.

During the early stages of the investigation an attempt was made to oxidize 1-iodo-2,6-difluoro-3,5-dimethylbenzene to the corresponding monocarboxy compound from which it was intended to prepare the corresponding diphenyl. The product was always the dicarboxy compound, which was unsuitable for production of a diphenyl with the proper structure. It was also impossible to isolate a partial oxidation product of 2,2′,6,6′-tetrafluoro-3,3′,5,5′-tetramethyldiphenyl.

2-Amino-3-methyl-5-chloro-6-nitrobenzene (IV).—In a 600-cc. beaker 20 g. of 2-amino-3-methyl-5-chlorobenzene (III) was dissolved in 200 g. of concentrated sulfuric acid. The mixture was cooled to 0–5° and to this was added dropwise, with stirring, 13 g. of concentrated nitric acid (sp. gr., 1.42). After all of the nitric acid had been added, the mixture was stirred for thirty minutes longer and poured onto ice. This caused a precipitation of the amine and the amine sulfate, which was filtered off, made alkaline and the free base purified from 40% alcohol, from which it crystallized in orange needles melting at 123–124° (corr.). The yield was 24.5 g. (93%).

Anal. Calcd. for $C_7H_7O_2N_2Cl$: N, 15.01. Found: (micro Dumas) N, 15.25.

The acetate was prepared by warming a small amount of the amine with acetic anhydride. From water, it formed long white needles, melting at 140–141° (corr.).

Anal. Calcd. for $C_9H_9O_3N_2Cl_2$: N, 12.22. Found: (micro Dumas) N, 12.31.

According to Reverdin and Crépieux[11] the acetate of this amine melted at 262°. They prepared it as follows: 2,6-dinitro-3-methyl-5-chlorobenzene was obtained by nitration of *m*-chlorotoluene. This was reduced with alcoholic ammoniacal sulfur dioxide solution to 2-amino-3-methyl-5-chloro-6-nitrobenzene melting at 120°. They give, however, no proof for the structure of their amine.

In order to prove definitely the structure of the acetate melting at 140–141° (corr.) the following procedure was carried out: (IV) was diazotized in 95% alcohol and boiled to remove the amino group in the 2 position, forming 3-methyl-5-chloro-6-nitrobenzene. This compound was reduced with stannous chloride and hydrochloric acid to 3-methyl-5-chloro-6-aminobenzene, which was treated with acetic anhydride to form the acetyl derivative. This compound was prepared before by Cohen and Dakin[12] and Klotz.[13] These authors reported its melting point as 113 and 114–115°, respectively. The melting point of the compound obtained above was found to be 114–115°.

3-Methyl-5-chloro-6-nitrobenzene-2-diazonium Borofluoride.—In a 300-cc. beaker was placed 25 cc. of concentrated hydrochloric acid containing a suspension of 15 g. of (IV). The mixture was cooled to 0° and a saturated solution of sodium nitrite was added slowly until all of the amine was in solution and until a slight excess of free nitrous acid was present (starch iodide test). The solution was filtered from sodium chloride and to the filtrate was added 28 g. of a solution of hydroborofluoric acid, made by mixing 20 g. of 48% hydrofluoric and 8 g. of boric acid. Upon addition of the acid, the borofluoride slowly crystallized out. The solution was allowed to stand for two hours at 0° and filtered. No purification was attempted. The yield was 14 g. (61%); dec. pt. 153° (corr.).

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[11] Reverdin and Crépieux, *Ber.*, **33**, 2507 (1900).

[12] Cohen and Dakin, *J. Chem. Soc.*, **81**, 1337 (1902).

[13] Klotz, *Ann.*, **231**, 311 (1885).

Anal. Calcd. for $C_7H_5O_2N_3Cl \cdot BF_4$: N, 14.70. Found: (micro Dumas) N, 15.64.

2-Fluoro-3-methyl-5-chloro-6-nitrobenzene (V).—The borofluoride just described was heated in small amounts (4–5 g.) *in vacuo* to 170°. The crude fluoride was distilled with steam from alkaline solution. The yield from 70 g. of borofluoride was 23 g. of fluoride (49.5%); b. p. 247° (750 mm.); m. p. 18–19°; n^{25}_{D} 1.5416; d^{25}_{25} 1.411.

Anal. Calcd. for $C_7H_5ClFNO_2$: N, 7.39. Found: (micro Dumas) N, 7.59.

2-Fluoro-3-methyl-5-chloro-6-aminobenzene (VI).—Five grams of V was reduced with stannous chloride[3] in a mixture of glacial acetic acid and concentrated hydrochloric acid. After complete reduction the solution was made alkaline with sodium hydroxide and the amine distilled from the reaction mixture. It formed shining white plates, which melted after crystallization from 50% alcohol at 55–56° (corr.); yield, quantitative.

Anal. Calcd. for C_7H_7NClF: N, 8.75. Found: (micro Dumas) N, 8.81.

The acetate formed by treatment of the base with acetic anhydride was crystallized from water, m. p. 138–139° (corr.).

Anal. Calcd. for C_9H_9ONClF: N, 6.96. Found: (micro Dumas) N, 7.14.

1-Acetoxy-mercuri-2-fluoro-3-methyl-5-chloro-6-aminobenzene (VII).—To a solution of 50 g. of VI in 250 cc. of absolute methyl alcohol was added 100 g. of mercuric acetate dissolved in 300 cc. of absolute methyl alcohol. After four hours the mixture was diluted with 700 cc. of water and allowed to stand overnight when VII separated out of solution in cotton-like needles. Purified from acetic acid it had a m. p. 216–218° (corr.) with dec.

Anal. Calcd. for $C_7H_6ClFN(HgOCOCH_3)$: Hg, 48.08. Found: (pptd. as HgS) Hg, 48.3.

1-Iodo-mercuri-2-fluoro-3-methyl-5-chloro-6-aminobenzene (VIII).—To a suspension of VII was added 116 g. of potassium iodide dissolved in 200 cc. of water and the mixture was warmed for thirty minutes on the steam-bath, which caused the formation of VIII. No means of purification was found; m. p. 275–279° (corr.), with dec. The crude product was used directly for the next step.

Anal. Calcd. for $C_7H_6ClFN(HgI)$: Hg, 41.35. Found: (pptd. as HgS) Hg, 41.65.

1-Iodo-2-fluoro-3-methyl-5-chloro-6-aminobenzene (IX).—To a suspension of VIII was added 500 cc. of methyl alcohol and 77 g. of iodine dissolved in 400 cc. of methyl alcohol. After adding the iodine the iodo derivative remained in solution and the mercuric iodide also as K_2HgI_4. The volume of the solution was reduced to one-half by evaporation and diluted with water, causing IX to separate in fine yellow needles. After purification from 60% methyl alcohol, m. p. 67–68° (corr.); yield, 78.5 g. (88% calcd. on VI).

Anal. Calcd. for C_7H_6NClF: N, 4.90. Found: (micro Dumas) N, 4.99.

The acetate prepared by dissolving the amine in acetic anhydride and adding several drops of concentrated sulfuric acid was purified by crystallization from 50% ethyl alcohol; m. p. 203–204° (corr.).

Anal. Calcd. for $C_9H_8NOIFCl$: N, 4.28. Found: (micro Dumas) N, 4.38.

In order to prove that the acetoxy-mercuri group was substituted in the 1 position, the following experiments were followed out. In glacial acetic acid, VI was brominated, using bromine dissolved in glacial acetic acid, yielding 1-bromo-2-fluoro-3-methyl-5-chloro-6-aminobenzene; m. p. 61–62° (corr.). A portion of VII was treated with an excess of aqueous sodium bromide solution forming 1-bromo-mercuri-2-fluoro-3-methyl-5-chloro-6-aminobenzene. This compound was treated with bromine in chloroform which caused the bromo-mercuri residue to be replaced by bromine. The compound obtained in this way melted at 61–62° (corr.), and a mixed melting point of the two showed no depression. Since these two compounds were identical, the acetoxy-mercuri group was in position 1 and hence the iodine of VIII is very probably in position 1.

1-Iodo-2-fluoro-3-methyl-5-chlorobenzene-6-diazonium-borofluoride.—This compound was prepared in a manner similar to the previously described borofluoride using IX as starting material. From 20 g. of the amine 18 g. of the borofluoride was obtained (65%), dec. pt. 218° (corr.).

Anal. Calcd. for $C_7H_4BClF_4IN_2$: N, 7.68. Found: (micro Dumas) N, 8.09.

1-Iodo-2,6-difluoro-3-methyl-5-chlorobenzene (X).—The decomposition of the borofluoride was carried out as described for other borofluorides. The temperature of decomposition was 220°. X was purified by distillation, b. p. 244–246° (corr.). From 20 g. of the borofluoride, 13 g. of the fluoride was obtained (85%). This was converted directly into the diphenyl.

2,2',6,6'-Tetrafluoro-3,3'-dimethyl-5,5'-dichlorodiphenyl (XI).—A mixture of 1 g. of X and 1 g. of activated copper was treated for two hours at 200°. The mixture was extracted with acetone, treated with norite and filtered. Water was added to help precipitate the crude diphenyl, which was crystallized from alcohol; m. p. 137–138° (corr.); yield, 0.3 g. (34%).

Anal. Calcd. for $C_{14}H_8Cl_2F_4$: Cl, 21.90. Found: (micro) Cl, 22.16.

2,2',6,6'-Tetrafluoro-3,3'-dicarboxy-5,5'-dichlorodiphenyl (I).—A mixture of 0.5 g. of XI and 4 cc. of concentrated nitric acid diluted with 14 cc. of water was heated at 160° for twenty hours in a sealed tube. The acid was dissolved in sodium hydroxide solution and filtered from any unreacted diphenyl. The acid was reprecipitated with dilute sulfuric acid and crystallized from 50% alcohol; fine needles, m. p. 295–298° (corr.) with shrinking at 285°. The yield was 0.5 g. (84.5%).

Anal. Calcd. for $C_{14}H_4O_4Cl_2F_4$: Cl, 18.44; n. e., 172.5. Found: (micro) Cl, 18.54; n. e., 171.9.

ATTEMPTED RESOLUTION OF I

Salt	Wt. to 10 cc. in alcohol, g.	$l = 1$ α_D	$[\alpha]_D^0$	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Cinchonidine	0.1000	−0.65°	−65°	$C_{14}H_4O_4F_4Cl_2 \cdot C_{19}H_{22}ON_2$	4.37	4.60
Strychnine	.1500	− .64	−42.7	$C_{14}H_4O_4F_4Cl_2 \cdot (C_{21}H_{22}N_2O_2)_2$	5.33	5.39
Morphine	.1500	−1.35	−90	$C_{14}H_4O_4F_4Cl_2 \cdot (C_{17}H_{19}NO_3)_2$	2.93	3.05

The salts were prepared in alcohol. The cinchonidine salt was precipitated fractionally from alcohol by addition of ether. The strychnine salt was fractionated from chloroform; the morphine salt from acetone. All fractions of each salt gave the same rotation, no mutarotation and on decomposition gave inactive acids.

1-Acetoxy-mercuri-2-fluoro-3,5-dimethyl-6-aminobenzene.—To a solution of 50 g. of 2-fluoro-3,5-dimethyl-6-aminobenzene[10] in 250 cc. of absolute methyl alcohol was added 100 g. of mercuric acetate dissolved in 300 cc. of absolute methyl alcohol. The mixture was allowed to stand four hours and then diluted with 700 cc. of water and allowed to stand overnight in a cool place when 1-acetoxy-mercuri-2-fluoro-3,5-dimethyl-

6-aminobenzene separated out of solution in fine needles. Purified from acetic acid it had a melting point of 207–208° (corr.) with dec.

Anal. Calcd. for $C_8H_9FN(HgOCOCH_3)$: Hg, 50.6. Found: (pptd. as HgS) Hg, 50.9.

1-Iodo-mercuri-2-fluoro-3,5-dimethyl-6-aminobenzene.—A suspension of 50 g. of the 1-acetoxy-mercuri compound in water was treated with 58 g. of potassium iodide. The mixture was heated, causing the precipitation of the insoluble mercuric iodide derivative which melted with decomposition at 235–240° (corr.). The yield was quantitative.

Anal. Calcd. for $C_8H_9FN(HgI)$: Hg, 43.13. Found: (pptd. as HgS) Hg, 43.50.

1-Iodo-2-fluoro-3,5-dimethyl-6-aminobenzene.—To the aqueous methyl alcoholic suspension of 1-iodo-mercuri-2-fluoro-3,5-dimethyl-6-aminobenzene from the above preparation was added 80 g. of iodine dissolved in 400 cc. of methyl alcohol. After cooling, the mercuric iodide precipitated out and the product remained in solution. After filtration the methyl alcohol was distilled off and the compound crystallized from 50% alcohol, m. p. 53–54°.

Anal. Calcd. for C_8H_9FIN: I, 47.92. Found: (micro Dumas) I, 48.15.

In order to prove that the acetoxy-mercuri group had substituted in position 1, the compound obtained by bromination of 2-fluoro-3,5-dimethyl-6-aminobenzene in glacial acetic acid was compared with the compound obtained by treating 1-acetoxy-mercuri-2-fluoro-3,5-dimethyl-6-aminobenzene with aqueous sodium bromide and then with bromine in chloroform. Both of these compounds melted at 56° (corr.) and the mixed melting point showed no depression. This compound, 1-bromo-2-fluoro-3,5-dimethyl-6-aminobenzene, had been previously described by Becker and Adams.[10]

1-Iodo-2-fluoro-3,5-dimethylbenzene-6-diazonium Borofluoride.—As described previously for analogous compounds, 1-iodo-2-fluoro-3,5-dimethyl-6-aminobenzene was converted to the borofluoride. From 20 g. of the amine 17 g. of the borofluoride was obtained (65%); dec. pt. 235° (corr.).

1-Iodo-2,6-difluoro-3,5-dimethylbenzene.—The decomposition of the borofluoride was carried out in a 500-cc. distillation flask heated to 200° to which was connected a reflux condenser. From 10 g. of borofluoride 5.5 g. of fluoride was obtained (75%). The fluoride was purified by steam distillation and by crystallization from low-boiling petroleum ether; m. p. 42–43° (corr.).

Anal. Calcd. for $C_8H_7F_2I$: I, 47.5. Found: (micro Dumas) I, 47.8.

1-Iodo-2,6-difluoro-3,5-dicarboxybenzene.—A mixture of 2 g. of 1-iodo-2,6-difluoro-3,5-dimethylbenzene and 10 cc. of nitric acid (sp. gr., 1.42) diluted with 20 cc. of water was heated in a sealed tube for thirty-six hours at 160°. The purpose of the preparation was to produce 1-iodo-2,6-difluoro-3-methyl-5-carboxybenzene, but in no case could any monocarboxylic acid be isolated. The dicarboxylic acid was crystallized from water. The yield was 2 g. (85%); m. p. 223–226°.

Anal. Calcd. for $C_8H_3O_4F_2I$: I, 38.7. Found: (micro Dumas) I, 39.2.

2,2′-6,6′-Tetrafluoro-3,3′,5,5′-tetramethyldiphenyl.—A mixture of 2 g. of 1-iodo-2,6-difluoro-3,5-dimethylbenzene and 2 g. of active copper was heated for two hours at 200°. The mixture was extracted with acetone and filtered. Water was added to precipitate the crude diphenyl, which was crystallized from 70% alcohol. The yield was 0.63 g. (60%); m. p. 149–150° (corr.). The analysis of this compound is interesting since it was the only case in this investigation in which the carbon and hydrogen determinations of a fluorinated compound gave satisfactory results.

Anal. Calcd. for $C_{16}H_{14}F_4$: C, 68.15; H, 4.97. Found: (micro) C, 68.36; H, 4.90.

Copper Bronze.—Ordinary copper bronze sometimes gave very satisfactory and sometimes very poor results in the Ullmann condensation. A simple treatment of the commercial copper bronze made possible more uniform results and frequently made possible a more rapid reaction at a lower temperature.

The copper bronze was treated with a 2% solution of iodine in acetone for about five to ten minutes. This caused it to turn rather grayish in color due to the formation of copper iodide. The product was filtered and treated with dilute hydrochloric acid in acetone. The copper iodide dissolved and the copper bronze remaining was filtered and washed with acetone. It was then dried in a vacuum desiccator. It was found preferable to use this bronze immediately after preparation.

Analysis of Organic Mercury Compounds.—Analyses for mercury were made by a combination of two methods. For the decomposition of the organic mercury compound the method of Tabern[14] was used. The determination of the soluble mercury compound was made through hydrogen sulfide precipitation and weighing of the mercuric sulfide.

Summary

1. 2,2′6,6′-Tetrafluoro-3,3′-dicarboxy-5,5′-dichlorodiphenyl has been prepared. It could not be resolved. The structure of this molecule and of others of a similar character has been discussed.

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[14] Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

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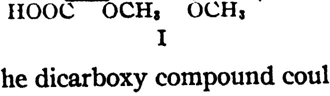
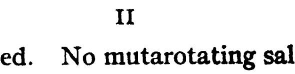
Stereochemistry of Diphenyls. XXXII.[1] Preparation and Properties of Certain 2,2′,6,6′-Tetramethoxydiphenyls

BY A. M. VANARENDONK,[2] M. E. CUPERY AND ROGER ADAMS

Simultaneously with the preparation and study of the 2,2′,6,6′-tetrafluorodiphenyl described in the previous paper in this series, the synthesis of 2,2′,6,6′-tetramethoxydiphenyls has been undertaken. Two compounds 2,2′,6,6′-tetramethoxy-3,3′-dicarboxydiphenyl (I) and 2,2′,6,6′-tetramethoxy-3,3-diaminodiphenyl (II) have been produced and the properties determined.



I



II

The dicarboxy compound could not be resolved. No mutarotating salts could be obtained even at −17° and no active acid by decomposition of any of the salts.

Resolution of the diamino compound was attempted through the dicamphorsulfonate. At 0° the salt showed a rapid mutarotation. On the other hand, if the salt was dissolved as quickly as possible in methyl alcohol at −17° and the rotation determined at that temperature, readings of the mutarotation could readily be recorded. Although necessarily qualitative in character, several repetitions of the experiment gave the same results. It would appear, then, that four methoxyl groups represent about the lower limit for obtaining restricted rotation in the diphenyl molecules at temperatures above −17°. On the basis of calculations previously used for relative interference values, the internuclear distance from the carbon of the ring to the center of the methoxyl group is approximately 1.45 Å. A similar conclusion may be drawn from the results of this investigation.

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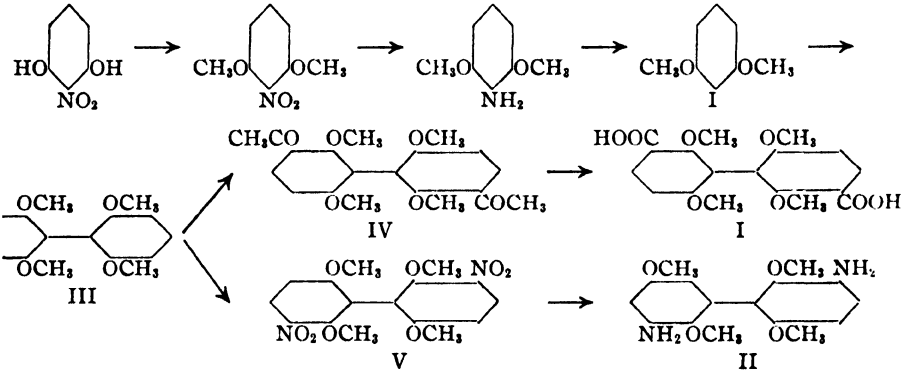
[1] For the previous paper in this series see Kleiderer and Adams, THIS JOURNAL, **55**, 4219 (1933); see also Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

[2] Submitted as part of a thesis for the Degree of Doctor of Philosophy at the University of Illinois.

By comparing the racemization rates of 2,2′-difluoro-6,6′-dicarboxydiphenyl;[3] 2,2′-difluoro-6,6′-diamino-3,5,3′,5′-tetramethyldiphenyl;[4] 2-nitro-6-carboxy-2′-methoxydiphenyl;[5] 2-nitro-6-carboxy-2′-fluorodiphenyl[5] and 2,2′-dimethoxy-6,6′-dicarboxydiphenyl[3,6] it may be concluded that the methoxyl group is substantially larger than the fluorine and substantially smaller than the amino group so far as concerns interference effects in the diphenyl molecules.

Experimental

The two compounds studied were produced by the following series of reactions.


HO OH NO₂
CH₃O OCH₃ NO₂
CH₃O OCH₃ NH₂
CH₃O OCH₃ I
OCH₃ OCH₃ OCH₃ OCH₃
III
CH₃CO OCH₃ OCH₃ OCH₃ OCH₃ COCH₃
IV
HOOC OCH₃ OCH₃ OCH₃ OCH₃ COOH
I
OCH₃ OCH₃ NO₂ NO₂ OCH₃ OCH₃
V
OCH₃ OCH₃ NH₂ NH₂ OCH₃ OCH₃
II

2-Iodo-1,3-resorcinol Dimethyl Ether.—This compound has been previously described[7] but modifications in the various steps as used in this investigation will be outlined briefly.

(A) 2-Nitro-1,3-resorcinol.—Resorcinol was nitrated as described by Kaufmann and de Pay[8] except that it was first dissolved in cold concentrated sulfuric acid.

(B) 2-Nitro-1,3-resorcinol Dimethyl Ether.—A solution of 50 g. of dry 2-nitroresorcinol in 300 cc. of dry toluene was heated to boiling and 80 cc. of dimethyl sulfate

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(3) Stanley, McMahon and Adams, THIS JOURNAL, **55**, 706 (1933).

(4) Kleiderer and Adams, *ibid.*, **53**, 1575 (1931).

(5) Stoughton and Adams, *ibid.*, **54**, 4426 (1932).

(6) Kenner and Turner, *J. Chem. Soc.*, 2340 (1928).

(7) Kaufmann and Franck, *Ber.*, **40**, 4014 (1907); Baeyer, *Ann.*, **372**, 127 (1910).

(8) Kaufmann and de Pay, *Ber.*, **37**, 726 (1904).

added. At about 100° with stirring 100 g. of finely powdered anhydrous potassium bicarbonate was added in small amounts sufficient to produce a brisk evolution of carbon dioxide. After fifteen minutes about 2 cc. of water was carefully added with the solution temperature at 100°. The stirring was continued for one hour with the temperature at 90–100°. Another 15 cc. of dimethyl sulfate was added with another small amount of water, and the heating continued until the solid material in the flask became nearly white (fifteen to thirty minutes). At this point 5 g. of powdered sodium carbonate was added to destroy any excess of dimethyl sulfate, and stirring and heating continued for about fifteen minutes. The hot solution was filtered, the toluene removed by distillation under reduced pressure and the solid residue dissolved in 150 cc. of hot butyl alcohol. After treatment with norite, 2-nitro-1,3-resorcinol dimethyl ether separated upon cooling. Another butyl alcohol–norite treatment followed by crystallization from 80% alcohol gave white crystals, m. p. 130°, yield 83%.

(C) 2-Amino-1,3-resorcinol Dimethyl Ether.—The nitro compound was reduced catalytically[9] in alcohol with platinum oxide and hydrogen at a pressure of 2–3 atm.; yield quantitative.

(D) 2-Iodo-1,3-resorcinol Dimethyl Ether.—The iodo compound was made as described by Kaufmann and Franck[10] except that the amine was dissolved in 95% acetic acid containing excess over the theoretical of concentrated sulfuric acid; m. p. 102–103°; yield 85%.

2,2′,6,6′-Tetramethoxydiphenyl (III).—A mixture of 15 g. of pure powdered 2-iodo-1,3-resorcinol dimethyl ether and 45 g. of very finely divided copper bronze was tightly packed into a large Pyrex test-tube and covered with a layer of copper bronze. A closely fitting cork stopper was then inserted into the tube directly above the reaction mixture. The tube was heated in an oil-bath, the temperature of which was 170–200° for two to three hours and finally 210° for fifteen minutes. After cooling, the reaction mixture was extracted in a Soxhlet apparatus with acetone for twenty hours. The tetramethoxydiphenyl crystallized from the acetone on cooling. The 2,2′,6,6′-tetramethoxydiphenyl is easily purified by recrystallization from acetone containing a little water; m. p. 175–176°, yield 6–7 g. (85–90%).

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.03; H, 6.62. Found: C, 69.76; H, 6.78.

The tetramethoxydiphenyl was also prepared by means of the Grignard reaction, by treatment with anhydrous cupric chloride. The yield was much lower than in the Ullmann reaction, but the compound proved to be identical in every way.

2,2′,6,6′-Tetramethoxy-3,3′-diacetodiphenyl (IV).—A mixture of 5 g. of pure tetramethoxydiphenyl, 75 cc. of dry carbon disulfide and 25 cc. of acetyl chloride was placed in a 3-necked flask with a mechanical stirrer and a thermometer. After cooling by means of an ice-bath, 5 g. of anhydrous ferric chloride was added with vigorous stirring followed in a few minutes by another equal amount. Stirring was continued vigorously for fifteen to twenty minutes. The flask was allowed to warm gradually to about 30° and stirring was continued for about half an hour, until a brown pasty mass settled to the bottom of the flask. The carbon disulfide solution was decanted and discarded. The residue was added to warm water, then well cooled and filtered. The solid was dissolved in a small quantity of alcohol and the colloidal ferric chloride removed by adding a small portion of sodium hydroxide and filtering.

The product can be crystallized from dilute alcohol but it is necessary to allow the solution to stand in a refrigerator for several days. If the alcohol is too dilute the diaceto compound may separate as an oil and may also be recrystallized from an ethyl acetate solution to which an equal volume of petroleum ether has been added. The pure com-

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(9) "Organic Syntheses," Coll. Vol. I, (1932), pp. 53, 235, 452.

(10) Kaufmann and Franck, *Ber.*, **39**, 2724 1906.

pound is perfectly white and has m. p. 113–115°. The yields in this preparation varied widely and detailed directions were not discovered that would assure constant results.

As the diaceto derivative is not very easily purified by crystallization it was generally oxidized in a crude state.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.01; H, 6.19. Found: C, 67.15; H, 6.34.

2,2′,6,6′-Tetramethoxy-3,3′-dicarboxydiphenyl (I).—The crude diaceto compound was oxidized as described by Cupery and VanArendonk.[11] From 5 g. of diaceto compound, 75 cc. of methanol, 15 cc. of 20% sodium hydroxide solution and excess hypochlorite, there was obtained 2 g. of dibasic acid.

The 2,2′,6,6′-tetramethoxy-3,3′-dicarboxydiphenyl has one molecule of water of crystallization. It may be further purified by drying in an oven at 110° overnight, and then recrystallizing it from absolute ethyl acetate. It crystallized with one molecule of ethyl acetate, which was removed by heating in an oven at 125° for several hours, m. p. 231–232°.

Anal. Calcd. for $C_{18}H_{18}O_8 \cdot H_2O$: H_2O, 4.74. Found: H_2O, 4.89. Calcd. for $C_{18}H_{18}O_8 \cdot CH_3CO_2C_2H_5$: $CH_3CO_2C_2H_5$, 19.56. Found: $CH_3CO_2C_2H_5$, 19.76. Calcd. for $C_{18}H_{18}O_8$: neut. equiv., 362; C, 59.64; H, 5.01. Found: neut. equiv., 367; C, 59.56; H, 5.34.

Attempted Resolution of I

Salt	Weight	Made up to in chloroform, cc.	$l = 2$ α_D	$[\alpha]^{20}_D$
Brucine	0.1500	15	−0.36°	− 18°
Strychnine	.1500	15	−1.04	− 52
Cinchonine	.0500	10	+1.08	+108

All salts were very soluble in water and in many organic solvents. The free acid was difficult to obtain from the salts since in acid solution the free acid loses carbon dioxide on heating. The brucine salt was prepared in absolute ethanol from anhydrous brucine and anhydrous acid and fractionally precipitated by adding carbon tetrachloride. It may be recrystallized from a 1:2 mixture of pyridine and carbon tetrachloride. The strychnine and cinchonine salts were formed in alcohol solution, the solution evaporated to dryness and treated with ethyl acetate. All salts gave fractions with the same rotation, showed no mutarotation and gave inactive acids on decomposition.

2,2′,6,6′-Tetramethoxy-3,3′-dichloro-5,5′-dicarboxydiphenyl.—Into a solution of 1 g. of tetramethoxydiacetodiphenyl and a small quantity of iodine in 25 cc. of glacial acetic acid chlorine was slowly passed for several hours. The mixture was then slowly poured into cold aqueous sodium bisulfite. A heavy precipitate formed which was filtered. On warming to room temperature the substance became very sticky and no method was discovered for purification. It was, therefore, oxidized directly to the dibasic acid according to the method of Cupery and VanArendonk.[11]

The crude product was dried in an oven at 105° and gave a hard brown mass. This was dissolved in anhydrous ethyl acetate and filtered. Upon adding three volumes of petroleum ether, and allowing to stand in a cool place overnight, white crystals formed, m. p. 202–203°. A portion was recrystallized from ethyl acetate and petroleum ether and gave the same melting point.

Anal. Calcd. for $C_{18}H_{16}O_8Cl_2$: neut. equiv., 433; Cl, 16.6. Found: neut. equiv., 438; Cl, 17.1.

2,2′,6,6′-Tetramethoxy-3,3′-dinitrodiphenyl (V).—To 1 g. of 2,2′,6,6′-tetramethoxydiphenyl was added a mixture of 10 cc. of acetic anhydride and 0.6 cc. of concentrated nitric acid. The latter was prepared by warming fuming nitric acid (sp. gr. 1.5) until

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(11) Cupery and VanArendonk, This Journal, 53, 3184 (1931).

colorless. The mixture was heated until the reaction started, which was evidenced by a violent boiling, and a slight evolution of nitrogen dioxide fumes. When the boiling had ceased, the solution was heated on a hot-plate to incipient boiling for five minutes and was then allowed to stand for four hours at room temperature. An equal volume of water was added, and the mixture was heated slightly to decompose the acetic anhydride. Upon cooling the solution, an orange-colored precipitate was obtained which weighed 1 g. This was recrystallized several times from a minimum amount of hot alcohol and acetone mixture (1:1) with norite; white crystals, m. p. 174°; yield 0.7 g.

Anal. Calcd. for $C_{16}H_{16}O_8N_2$: C, 52.75; H, 4.40; N, 7.69. Found: (micro) C, 52.93; H, 4.52; N, 7.64.

2,2′,6,6′-Tetramethoxy-3,3′-diaminodiphenyl (II).—A mixture of 3 g. of carefully purified 2,2′,6,6′-tetramethoxy-3,3′-dinitrodiphenyl in 150 cc. of alcohol was heated to 50° and reduced with platinum oxide catalyst and hydrogen at 40 lb. pressure. The solution after filtration of the catalyst was evaporated under reduced pressure to 20 cc. and cooled in an ice-bath, whereupon practically all of the diamino compound precipitated. The diamine was recrystallized twice from hot alcohol to a perfectly white compound, m. p. 159–160°. Upon standing exposed to the air, the compound colored slightly, but this did not affect the melting point; yield, 2.3 g. (95%).

Anal. Calcd. for $C_{16}H_{20}O_4N_2$: C, 63.16; H, 6.58; N, 9.21. Found: (micro) C, 63.36; H, 6.62; N, 9.45.

Attempted Resolution of 2,2′,6,6′-Tetramethoxy-3,3′-diaminodiphenyl.—A solution of 1.1 g. of the diphenyl in 40 cc. of acetone was added to 1.5 g. of *d*-camphorsulfonic acid in 70 cc. of acetone. The solution was heated to boiling for one-half minute and allowed to cool to room temperature and to evaporate slowly. After three days, 0.2 g. of fine crystals was obtained. These were very dark brown in color, and the rotation could not be determined. On further standing, 0.8 g. of fine, white, powdery crystals separated, which softened at 220° and melted at 229–232° (uncorr.).

Anal. Calcd. for $C_{36}H_{52}O_{12}N_2S_2$: C, 56.25; H, 6.79; N, 3.65. Found: (micro) C, 56.40; H, 6.99; N, 3.71.

Mutarotation was so rapid that no very accurate values could be obtained at 0°. By working rapidly at −17° the initial reading could be taken in one and one-half minutes. Several determinations showed mutarotation in each instance though the results were too qualitative to warrant determination of the half life period.

Rotation. 0.04 g. of substance made up to 10 cc. in methanol gave at −17° α_D +0.34, $l = 1$; $[\alpha]^{-17}_D$ +85°; in less than two minutes α_D +0.13, $l = 1$; $[\alpha]^{-17}_D$ +32.5 which remained constant.

2,2′,6,6′-Tetraacetoxydiphenyl.—A solution of 2 g. of tetramethoxydiphenyl in 100 g. of glacial acetic acid and 8 g. of 40% hydrobromic acid was refluxed for nine hours and then allowed to stand overnight. Upon concentration to 3–4 cc. under reduced pressure, a thick viscous liquid remained which could not be crystallized. About 15 cc. of acetic anhydride was added and this solution kept just below boiling temperature for one hour. After cooling, water was added and the white solid obtained was purified by recrystallization from alcohol as white needles, m. p. 190°.

Anal. Calcd. for $C_{20}H_{18}O_8$: C, 62.15; H, 4.69. Found: C, 62.15; H, 5.01.

2,2′,6,6′-Tetramethoxy-3,3′,5,5′-tetranitrodiphenyl.—One gram of tetramethoxydiphenyl was gradually added with stirring to 20 g. of fuming nitric acid at 0°. Upon standing for two hours, the colored solution cleared to a pale yellow and was then poured into cold water. The product after several recrystallizations from acetic acid formed needle crystals, m. p. 194–195°.

Anal. Calcd. for $C_{16}H_{14}O_{12}N_4$: C, 42.09; H, 3.53. Found: C, 42.25; H, 3.38.

2,2',6,6'-Tetramethoxy-3,3',5,5'-tetraacetodiphenyl.—To a solution of 2 g. of tetramethoxydiphenyl in 30 cc. of hot acetic anhydride was added 4 g. of anhydrous aluminum bromide. The solution was gently refluxed for two hours and about 50 cc. of alcohol then added through the condenser. The solution was concentrated to about 30 cc., an equal volume of alcohol was added and the warm solution filtered. The white solid residue was dissolved in hot 10% sodium hydroxide, filtered, and reprecipitated with acetic acid. It was purified from glacial acetic acid, white crystals, m. p. with dec. 340–350°.

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 65.13; H, 5.92. Found: C, 65.15; H, 5.64.

Summary

2,2',6,6'-Tetramethoxy-3,3'-dicarboxydiphenyl and 2,2',6,6'-tetramethoxy-3,3'-diaminodiphenyl have been prepared. The former could not be resolved and no mutarotation of the salts was observed. The latter gave a dicamphorsulfonate that mutarotated at −17°.

Urbana, Illinois

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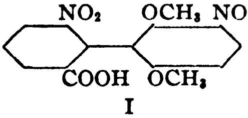
[Contribution from the Chemical Laboratory of the University of Illinois]

Stereochemistry of Diphenyls. XXXIII.[1] Preparation and Properties of 2,3'-Dinitro-6-carboxy-2',6'-dimethoxydiphenyl and 2-Nitro-6-carboxy-2'-fluoro-6'-methoxydiphenyl

By A. M. VanArendonk,[2] B. C. Becker and Roger Adams

In previous papers a description of the properties of 2,2',6,6'-tetrafluoro-3,3'-dichloro-5,5'-dicarboxydiphenyl;[3] 2,2',6,6'-tetramethoxy-3,3'-dicarboxydiphenyl;[1] 2,2',6,6'-tetramethoxy-3,3'-diaminodiphenyl;[1] and 2,2'-difluoro-6,6'-dimethoxy-3,3'-dicarboxydiphenyl[4] has been given. None of these compounds could be resolved and only in the case of the 2,2',6,6'-tetramethoxy-3,3'-diaminodiphenyl was it possible to observe the mutarotation of a salt at a temperature of −17°.

In this investigation two compounds have been prepared in which the 2,6 substituents were represented, respectively, by one fluorine and one methoxyl and by two methoxyls, while the 2',6' groups were nitro and carboxyl. The specific compounds were 2,3'-dinitro-6-carboxy-2',6'-dimethoxydiphenyl (I) and 2-nitro-6-carboxy-2'-fluoro-6'-methoxydiphenyl (II).



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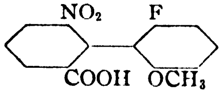
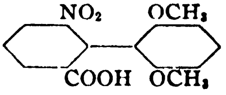


II



III

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(1) For previous papers in the series see VanArendonk, Cupery and Adams, This Journal, 55, 4225 (1933). See also Adams and Yuan, *Chem. Rev.*, 12, 261 (1933).

(2) Submitted as part of a thesis for the Degree of Doctor of Philosophy at the University of Illinois.

(3) Kleiderer and Adams, This Journal, 55, 4219 (1933).

(4) Becker and Adams, *ibid.*, 54, 2973 (1932).

Both compounds were readily resolved and the active compounds were racemized only under vigorous conditions. It is apparent that the relatively large size of the nitro and carboxyl groups in place of a fluorine and methoxyl in the non-resolvable compound containing 2,2′-difluoro-6,6′-dimethoxyl groups or in place of two methoxyls in the non-resolvable compound containing 2,2′,6,6′-tetramethoxyl groups has produced sufficient hindrance to prevent free rotation. The 2-nitro-6-carboxy-2′-fluoro-6′-methoxydiphenyl racemized more readily than the 2,3′-dinitro-6-carboxy-2′,6′-dimethoxydiphenyl, again indicating that the fluorine has less effect than the methoxyl.[1,3]

The general assumption has been accepted that in the stereochemistry of diphenyl each ring of the diphenyl must be unsymmetrically substituted in order to make possible resolution, even though restricted rotation is present in the molecule. The non-resolution of *o*-N-carbazylbenzoic acid but resolution of *o*-N-(3-nitrocarbazyl)-benzoic acid[5] confirmed this assumption in the phenylpyrrole series. In the diphenyl series, however, no compounds have been described in which restricted rotation would occur but in which symmetrical substitution was present, and at the same time salt-forming groups which would make possible attempts at resolution. The 2-nitro-6-carboxy-2′,6′-dimethoxydiphenyl (III) formed as an intermediate in the synthesis of I has such properties. Attempts to resolve it resulted in failure.

Experimental

III was produced by condensation of 2-nitro-1-iodo-3-carbethoxybenzene with 2-iodo-1,3-resorcinol dimethyl ether, then saponification, and I by subsequent nitration of III with concd. nitric acid in acetic acid. II was produced by condensing 2-nitro-1-bromo-3-carbethoxybenzene with 2-fluoro-1-iodo-3-methoxybenzene followed by saponification.

2-Nitro-6-carboxy-2′,6′-dimethoxydiphenyl (III).—A mixture of 56 g. of 2-iodo-1,3-resorcinol dimethyl ether and 38 g. of methyl 3-nitro-2-iodobenzoate was heated with stirring under reflux in a Woods metal bath to 240–250°, and 40 g. of finely divided copper was then slowly added (20 min.) the mixture being stirred during the addition. Fifteen minutes after the last addition of copper, 5 g. more of copper was added, and the heating continued for one-half hour with occasional stirring with a rod. At the end of the heating, the temperature was raised to 300° for five minutes. Then the mixture was allowed to cool slowly. The reaction mixture was boiled with 300 cc. of 95% alcohol and filtered. The residue was placed in a Soxhlet extractor, and was extracted overnight with 95% alcohol. The alcoholic solutions were then combined and evaporated to 100 cc. To this was added 200 cc. of 7% sodium hydroxide and the solution was refluxed for six hours. It was then diluted with 100 cc. of water and filtered, thus removing the alkali-insoluble tetramethoxydiphenyl. The filtrate was acidified with concentrated hydrochloric acid and the dark colored precipitate filtered off, washed several times with water and redissolved in sodium bicarbonate solution. A small amount of material remained undissolved and was filtered off. The bicarbonate solution was acidified and a tan precipitate settled out. After washing and drying it was recrystallized from a

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(5) Patterson and Adams, THIS JOURNAL, 55, 1069 (1933).

minimum amount of boiling glacial acetic acid to which was added a small amount of norite. Yellow crystals of 2-nitro-6-carboxy-2′,6′-dimethoxydiphenyl were obtained, m. p. 248–249° (uncorr.); yield, 5.4 g. (12%).

Anal. Calcd. for $C_{15}H_{13}O_6N$: C, 59.41; H, 4.29; N, 4.62; N. E., 296. Found: (micro) C, 59.60; H, 4.38; N, 4.61; N. E., 303.

The brucine, cinchonine, strychnine and cinchonidine salts were prepared in absolute alcohol and crystallized from the same solvent. Various fractions of each salt gave the same rotation. None showed mutarotation nor gave an active acid on decomposition.

Table I

Constants and Analyses of the Salts of 2-Nitro-6-carboxy-2′,6′-dimethoxydiphenyl

	Salt	M. p. (uncorr.), °C.	Wt., g.	α_D 15 cc. of dry $CHCl_3$ $l = 2$	$[\alpha]_D^{20°}$
1	Brucine	119–123	0.025	−0.044	− 13.2
2	Cinchonine	176–179	.025	+ .51	+153
3	Strychnine	126–132	.025	− .10	− 30.0
4	Cinchonidine	195–197	.025	− .23	− 69.0

		Analyses (micro), %					
		Carbon		Hydrogen		Nitrogen	
	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	$C_{38}H_{39}O_{10}N_3$	65.42	65.32	5.59	5.70	6.02	6.07
2	$C_{34}H_{35}O_7N_3$	68.34	68.30	5.86	6.04	7.03	7.06
3	$C_{36}H_{35}O_8N_3$	67.81	67.12	5.49	6.18	6.59	6.61
4	$C_{34}H_{35}O_7N_3$	68.34	68.29	5.86	5.80	7.03	7.07

2,3′-Dinitro-6-carboxy-2′,6′-dimethoxydiphenyl (I).—To 1 g. of III was added a mixture of 10 cc. of acetic anhydride and 0.2 cc. of nitric acid which was prepared by gently heating fuming nitric acid until colorless. The mixture was heated on a hot-plate until all of the solid dissolved and the liquid became orange colored. The solution was allowed to stand for two hours at room temperature and was then heated to incipient boiling for ten minutes. An equal volume of water was added to destroy the acetic anhydride and the solution was placed under an air jet and evaporated to a volume of 10–12 cc. Yellow needle-like crystals separated out. These were recrystallized from

Table II

Brucine Salts and Active Forms of 2,3′-Dinitro-6-carboxy-2′,6′-dimethoxydiphenyl

		Solvent for purif.	M. p., °C.	Solvent for rot.	α_D^{25} made up to 15 cc. $l = 2$	$[\alpha]_D^{25}$
1	Less sol. hydrated	Abs. alc. with a little acetone	146–152	Chloroform	+0.75	+225°
2	More sol. hydrated	Dil. alc.	142–148	Chloroform	− .756	−226.8°
3	*d*-Acid	Alcohol	174–175	Abs. alc.	+ .413	+123.9°
4	*l*-Acid	Alcohol	175–176	Abs. alc.	− .364	−109.2°

		Analyses, %			
		Carbon		Hydrogen	
	Formula	Calcd.	Found	Calcd.	Found
1	$C_{38}H_{38}O_{12}N_4$ (anhydrous)	61.62	61.59	5.14	5.36
2	$C_{38}H_{38}O_{12}N_4$ (anhydrous)	61.62	61.50	5.14	5.25

hot glacial acetic acid containing norite. White crystals of 2,3'-dinitro-6-carboxy-2',6'-dimethoxydiphenyl separated, m. p. 192–193° (uncorr.); yield, 0.8 g. (70%).

Anal. Calcd. for $C_{16}H_{12}O_8N_2$: C, 51.73; H, 3.44; N, 8.04. Found: (micro) C, 52.25; H, 3.59; N, 7.99.

The salts were made in absolute alcohol and fractionated apart in the same solvent. The free acids were obtained from the salts by treating at 0° with several portions of 6 *N* hydrochloric acid and allowing to stand for several hours.

Racemization Experiments.—0.050 g. made up to 15 cc. in glacial acetic acid gave α_D 1.235, $l = 2$; $[\alpha]^{20}_D$ +185.5°. After refluxing for eight hours the $[\alpha]^{20}_D$ was +32.4°. In boiling absolute ethyl alcohol no racemization in many hours could be observed; in aqueous sodium hydroxide or alcoholic sodium ethylate, decomposition gradually occurred.

2-Nitro-6-carboxy-2'-fluoro-6'-methoxydiphenyl (II).—A mixture of 20 g. of 1-fluoro-2-iodo-3-methoxybenzene[4] and 45 g. of 1-nitro-2-bromo-3-carbomethoxybenzene was stirred and heated under reflux at 210–240° for three hours during which 75 g. of copper bronze was added in small portions. The pasty mass after cooling was extracted with successive 50-cc. portions of hot 95% ethyl alcohol. The extracted solutions were filtered hot and combined, diluted to double volume with water, made strongly alkaline with 25 g. of sodium hydroxide in 150 cc. of water and heated to boiling for two hours in a flask fitted with a reflux condenser. The esters of dinitrodiphenic acid and fluoromethoxynitrocarboxydiphenyl were hydrolyzed by this treatment and upon further dilution stayed in solution as the sodium salts of the respective acids. The water solution of these salts was decanted from the insoluble difluorodimethoxydiphenyl, boiled with norite, filtered, and acidified with concentrated hydrochloric acid. The precipitated mixture of the monobasic and the dibasic acid was filtered off, partially dried by suction, dissolved in hot glacial acetic acid, filtered and cooled. The dinitrodiphenic acid separated while the monobasic acid remained in solution. This solution was evaporated to a small volume and again allowed to cool in order to remove the last traces of the dinitrodiphenic acid which was filtered off. The filtrate was now slowly diluted with water till no more gum precipitated. After decanting the solution further addition of water and concentrated hydrochloric acid caused the formation of light brown crystals which were purified from 50% ethyl or methyl alcohol, then from ethyl ether by the addition of petroleum ether (large crystals), and finally again from 50% ethyl alcohol; m. p. 173–174° (uncorr.); yield, 0.6 g.

Anal. Calcd. for $C_{14}H_{10}FNO_5$: C, 57.5; H, 3.44; N, 4.81. Found: (micro) C, 57.6; H, 3.69; N, 5.37.

Resolution of 2-Nitro-6-carboxy-2'-fluoro-6'-methoxydiphenyl.—The monobrucine salt was made in alcohol and the two diastereoisomers were obtained by fractionation. Both the less soluble and the more soluble salts were purified by recrystallization from alcohol. The salts were decomposed to the active acids by shaking for one hour with 5 cc. of concentrated hydrochloric acid, a little ice and a few drops of chloroform. The free acids precipitated and were recrystallized from 50% alcohol.

CONSTANTS OF SALTS AND ACIDS

		M. p., °C.	Wt. made up to 15 cc. in $CHCl_3$	$l = 2$ α_D	$[\alpha]^{25}_D$
1	Less sol. brucine salt	215	0.0388	+0.538°	+103.9°
2	More sol. brucine salt	207	.047	− .657°	−104.8
3	*d*-Acid	157	.0146 (alc.)	+ .12	+ 61.6
4	*l*-Acid	157	.0120 (alc.)	− .105	− 65.6

CONSTANTS OF SALTS AND ACIDS (*Concluded*)

	Formula	Analyses, %					
		Carbon		Hydrogen		Nitrogen	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
1	$C_{14}H_{10}FNO_5 \cdot C_{23}H_{26}N_2O_4$	64.8	65.3	5.2	5.5	6.13	6.06
2	$C_{14}H_{10}FNO_5 \cdot C_{23}H_{26}N_2O_4$	..	..	...	...	6.13	6.60
3	$C_{14}H_{10}FNO_5$	..	..	...	...	4.81	5.16
4	$C_{14}H_{10}FNO_5$	..	..	...	...	..	..

Racemization of *l*-acid. Initial α_D −0.36 in C_2H_5OH—Boiling gave the following α_D readings: fifteen minutes, 0.335; forty-five minutes, 0.25; seventy-five minutes, 0.20; one hundred and thirty-five minutes, 0.17. Calcd. half life period, eighty-six minutes. In boiling glacial acetic acid, rotation was zero in less than twenty minutes. In boiling chloroform, half life period was seventy-two minutes. The acids racemized very slowly in aqueous sodium hydroxide or alcoholic sodium ethylate at room temperature.

Summary

2,3′-Dinitro-6-carboxy-2′,6′-dimethoxydiphenyl and 2-nitro-6-carboxy-2′-fluoro-6′-methoxydiphenyl were prepared and resolved. The active forms of the former racemized less readily than those of the latter, showing the fluorine to have less effect in restricting rotation than the methoxyl.

URBANA, ILLINOIS

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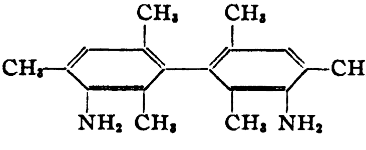
[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

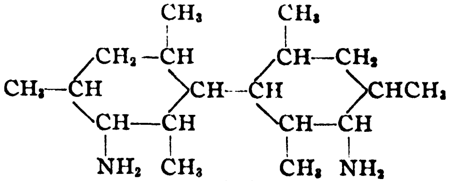
The Hydrogenation of Derivatives of Diphenyl

BY C. R. WALDELAND, WALTER ZARTMAN AND HOMER ADKINS

In connection with the stereochemistry of diphenyl derivatives it would be of interest to ascertain whether or not an optically active dicyclohexyl compound could be obtained by the hydrogenation of an optically active diphenyl compound. For example, if optically active 3,3′-diamino-2,2′,-4,4′,6,6′-hexamethyldicyclohexyl (II) resulted from the hydrogenation of the corresponding *d*- or *l*-diaminodimesityl (I), then the basis for the optical isomerism of compounds of type I is not some "inherent property" of the parent hydrocarbon.[1]



(I)



(II)

It appears that the most feasible way to discover whether derivatives of dicyclohexyl show optical isomerism based upon molecular asymmetry as distinguished from atomic asymmetry, is by such a conversion of optically active diphenyls into dicyclohexyls. This is true because a compound such as II, for example, contains ten asymmetric atoms and the number of isomers is thus too great to make it possible to distinguish readily between those dependent upon molecular and atomic asymmetry.

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[1] Turner and LeFèvre, *J. Soc. Chem. Ind.*, **45**, 831, 883 (1926); Turner, *Rec. trav. chim.*, **48**, 824 (1929); *cf.* Richter, *Chem. Rev.*, **10**, 368 (1932).

For the above reasons diaminodimesityl (I) was prepared and resolved.[2] It was then submitted to the conditions which ordinarily bring about a rapid hydrogenation of a benzenoid ring. When these conditions were found to produce no hydrogenation, the compound was then subjected to such drastic conditions as 350 atmospheres pressure of hydrogen at 225° for many hours in the presence of an equal weight of a very active nickel catalyst. The compound absorbed no hydrogen and was recovered practically unchanged in m.p. (201–202.5°) and molecular rotation after being repeatedly subjected to the drastic conditions described above.

The diethyl and dimethyl esters of 6,6′-dimethoxydiphenic acid were then prepared. The acid corresponding to the esters is readily resolvable but this operation was not carried out since it appeared unnecessary to do so until it had been ascertained whether the *dl* mixture would undergo hydrogenation. The *dl* mixture did not undergo hydrogenation to dicyclohexyl derivatives although repeated treatments with active nickel and hydrogen at 250° and 350 atmospheres in methylcyclohexane as a solvent resulted in the formation of small amounts of liquid products.

All of the resources of this Laboratory with respect to technique and equipment and all the experience in the use of nickel as a catalyst for hydrogenation have been of no avail for the hydrogenation of these two derivatives of diphenyl. Various types and preparations of nickel catalyst of known activity, various temperatures, pressures, solvents, time and ratios of catalyst to organic compound, etc., have alike yielded negative results.

In contrast with these *d* and *dl* compounds, 3,3′-dimethyl- and 4,4′-dimethyldiphenyl were readily hydrogenated to the corresponding dicyclohexyls. Diethyl diphenate was successfully hydrogenated to a mixture of isomeric 2,2′-dicarbethoxydicyclohexyls. 4,4′-Dihydroxydiphenyl was converted in a fair yield to the corresponding dicyclohexyl. Fluorenone which may also be regarded as a substituted diphenyl was also readily hydrogenated to dodecahydrofluorene. Dimesityl (a hexamethyldiphenyl) was previously hydrogenated to the corresponding hexamethyldicyclohexyl.[3] Among the many compounds which have been subjected to the conditions for catalytic hydrogenation in this Laboratory a few such as benzidene and 3,3′-diaminodiphenyl have not been successfully hydrogenated because of condensation or decomposition, but only the *d*- and *dl*-diphenyl derivatives referred to above have failed to react.

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[2] Adams and Moyer, THIS JOURNAL, **51**, 630 (1929).

[3] Adkins, Zartman and Cramer, *ibid.*, **53**, 1425 (1931).

It is possible that the same factors which prevent the rotation of the rings with respect to each other in resolvable derivatives of diphenyl, also prevent the reaction (adsorption) of the benzenoid ring by the catalyst, and so inhibit the first step in the catalytic hydrogenation of the former.

Experimental Part

The 3,3'- and 4,4'-dimethyldiphenyl[4] (18 g.) were quantitatively hydrogenated in five to six hours in methylcyclohexane at 200°, 100 atm., with 4 g. of ammonium carbonate type nickel catalyst to the corresponding 3,3'-dimethyldicyclohexyl, b. p. 254–256° (740 mm.)[5] and 4,4'-dimethyldicyclohexyl, b. p. 119–121° (10 mm.).[6] The 4,4'-dihydroxydiphenyl[7] (19 g.) was hydrogenated in twelve hours in ethanol at 200°, 100 atm., with two applications of catalyst of 5 g. each to 4,4'-dihydroxydicyclohexyl, m. p. 204–207° (78% yield), and 4-hydroxydicyclohexyl, m. p. 94–98° (22% yield). *Anal.* Calcd. for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19. Found: C, 73.08; H, 11.25. *Anal.* Calcd. for $C_{12}H_{22}O$: C, 79.04; H, 12.17. Found: C, 78.75; H, 12.16.[8]

The 4,4'-dimethoxydiphenyl[4] when subjected to hydrogenation as for the dihydroxy compound gave a 50% yield of 4-methoxydicyclohexyl, b. p. 120–121° (7 mm.), d_{25}^{25} 0.9394; n_D^{25} 1.4772, MR'$_D$, calcd. 58.86; found, 59.03. *Anal.* Calcd. for $C_{13}H_{24}O$: C, 79.51; N, 12.33. Found: C, 79.34; H, 12.29.

Diethyl diphenate (16 g.) in methylcyclohexane was hydrogenated twice at 200°, 100–165 atmospheres with 5 g. of a nickel catalyst. The product (13 g.) b. p. 167–170° (3 mm.) was a liquid n_D^{25} 1.4769, from which upon standing for twenty-four hours at 15° 3 g. of crystals separated. After recrystallization from ethanol, the solid had a m. p. of 84–85° and was presumably *trans* 2,2'-dicarbethoxydicyclohexyl. *Anal.* Calcd. for $C_{18}H_{30}O_4$: C, 69.68; H, 9.68. Found: C, 69.44; H, 9.54. The liquid and presumably *cis* isomer was then fractionated and 5.9 g. of a colorless viscous liquid b. p. 155–158° (1–2 mm.) was obtained: d_{24}^{24} 1.0438; n_D^{24} 1.4774; MR'$_D$ calcd. 84.23; found, 83.99. *Anal.* Found: C, 70.05; H, 9.61.

Many attempts have been made to hydrogenate benzidene but none of them have been successful (although considerable quantities of hydrogen were absorbed) because of the liberation of ammonia and the formation of high molecular weight compounds. In ethanol a 26% yield of N-tetraethylbenzidine (m. p. 85°) was obtained[9] while in methylcyclohexane a small yield of 4-aminodicyclohexyl was isolated.[10] The 3,3'-dinitrodiphenyl (25 g.) in ethanol was hydrogenated in a few minutes at 100 atmospheres, 100°, with 4 g. of nickel catalyst. The corresponding 3,3'-diaminodiphenyl was formed almost quantitatively.[11]

The 6,6'-dimethoxydiphenic acid was prepared by the same method with two exceptions as that used by Kenner and Turner.[12] The 2-nitro-3-methoxybenzoic acid was reduced with hydrogen and Adams platinum oxide catalyst in acetic acid instead of with ferrous ammonium sulfate, and the yields were thereby almost doubled over those reported by Kenner and Turner. The resulting aminomethoxybenzoic acid was converted to the corresponding diphenic acid by the method described for the preparation of diphenic acid by Huntress.[13] It is important that the diazotization be carried out at 35–37° and that the coupling reaction take place in the presence of a stirrer so designed that the surface as well as the body of the reaction mixture is thoroughly agitated. The yield of acid from the coupling reaction was 85% and after purification with zinc and acetic acid the m. p. (with decomposition) was 295–298°.

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[4] Gardner and Borgstrom, THIS JOURNAL, **51**, 3376 (1929).

[5] Kursanoff, *J. Russ. Phys.-Chem. Soc.*, **34**, 224 (1902); *Chem. Centr.*, 1228 (1902).

[6] Tschitschibabin and Jelgasin, *J. Russ. Phys.-Chem. Soc.*, **46**, 812 (1914); *Chem. Centr.*, 875 (1915).

[7] Hunter and Woollett, THIS JOURNAL, **43**, 149 (1921).

[8] Schrauth, *Ber.*, **56**, 1905 (1923), reported m. p. for the *cis* 83°, for the *trans* 105°.

[9] Hoffman, *Ann.*, **115**, 366 (1860).

[10] Kursanoff, *ibid.*, **318**, 324 (1901).

[11] Brunner, *Ber.*, **20**, 1028 (1887).

[12] Kenner and Turner, *J. Chem. Soc.*, 2340 (1928).

Summary

A number of derivatives of diphenyl have been subjected to the conditions for catalytic hydrogenation to the corresponding dicyclohexyls. Reaction ensued with all the compounds except the two which possessed the structure necessary for molecular asymmetry and they resisted hydrogenation even under very drastic conditions.

[13] Huntress, "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 30.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 93]

The Influence of Branched Chains on Optical Activity. The Configuration of Methyl-tertiary-butylcarbinol

BY PHILIP G. STEVENS

In a recent paper[1] it was shown that in an homologous series of secondary carbinols, a change of a propyl to an isopropyl group caused a shift of the optical rotation in the opposite direction from that of the propyl carbinol. In the case of methylisopropylcarbinol, the shift was insufficient to change the sign of rotation; but with the other members, ethyl-, propyl- and butylisopropylcarbinols, the shift was accompanied by a reversal of the sign of rotation. It can be seen that if a branched chain (isopropyl group) directly attached to the asymmetric carbon atom causes a shift of the rotation in the opposite direction, a further branching of the chain (tertiary-butyl group) might cause an even greater shift, possibly sufficient to invert the sign of rotation even of the first member of the series.

The correlation of methyl-tertiary-butylcarbinol was therefore undertaken in order to complete the study of the effect of the branched chain on the optical rotation. The only sure method of correlation is by direct chemical means as in the case of methylisopropylcarbinol. The case of methyl-tertiary-butylcarbinol is however a much more difficult one, and up to the present time no direct chemical method has been found.

The only recourse therefore is correlation by means of Freudenberg's Displacement Rule. Freudenberg[2] has already assigned dextro methyl-tertiary-butylcarbinol as related to the other dextro carbinols. This tentative correlation, however, rests solely upon the rotation of the phthalate, and according to Freudenberg[3] himself, it cannot be considered as rigorous, for the Displacement Rule does not allow that carbinols be compared with their ethers or esters.[4] Consequently an attempt has been made here to abide by all the laws of the Displacement Rule.

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[1] Stevens, THIS JOURNAL, 54, 3732 (1932).

[2] Freudenberg, "Stereochemie," 1932, p. 696.

The correlation of methyl-tertiary-butylcarbinol was accomplished by comparing the rotations of its acetate, benzoate and phthalate and those of methylisopropylcarbinol and methyl-*n*-butylcarbinol, two closely related carbinols.

	CH_3	Carbinol	Acetate	[M] Benzoate	Phthalate
	C_3H_7-*n*	+12.1[5]	+22.3[5]		+95 ($CHCl_3$)[5]
A	C_3H_7-*i*	+ 4.3[5]	+24.6		+89.3 ($CHCl_3$)[5]
	C_4H_9-*n*	+12.0[5]	+17.0[5]		+117.5 (C_2H_5OH)[5]
B	C_4H_9-*n*	+12.0[5]	+17.0[5]		+117.5 (C_2H_5OH)[5]
	C_4H_9-*t*	+7.8[5]	+25.5		+159.7 ($CHCl_3$)[5]
	C_3H_7-*i*	+4.3[5]	+24.6	+79.8°	
C				+74.3 ($CHCl_3$)	+89.3 ($CHCl_3$)[5]
	C_4H_9-*t*	+7.8[5]	+25.5	+93.4	+159.7 ($CHCl_3$)[5]
				+86.3 ($CHCl_3$)	

In the upper set A are compared the acetates and phthalates of three carbinols whose configurations have been determined by direct chemical means. In every case there is a dextro shift proceeding from the acetates to the phthalates. Examining the next two sets, B and C, in which methyl-tertiary-butylcarbinol is compared with methyl-*n*-butylcarbinol and methylisopropylcarbinol, respectively, it is seen that the same relations exist, *e. g.*, a dextro shift from the acetates to the phthalates, and from the acetates through the benzoates to the phthalates. If methyl-tertiary-butylcarbinol had the opposite configuration, then in B and C the shift would be levo, quite out of line with the other carbinols. Therefore according to the Displacement Rule, methyl-tertiary-butyl-, methylisopropyl- and methyl-*n*-butylcarbinols are configurationally related when all have the same sign of rotation.

CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
HCOH	HCOH	HCOH	HCOH	HCOH	HCOH	HCOH	HCOH
C_3H_7-*n*	C_3H-i_7	C_4H_9-*n*	C_4H_9-*t*	C_4H_9-*i*	C_6H_{13}-*n*	C_6H_{11}	C_6H_5
[M] +12.1[5]	+4.3[5]	+12.0[5]	+7.8[5]	+21.1[6]	+12.7[5]	+6.5[7] (+7.3)[8,9]	−52.5[5,9]

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[3] Freudenberg, *Ber.*, **66**, 177 (1933).

[4] This condition rules out the criticism of the Displacement Rule by Levene and Marker [*J. Biol. Chem.*, **97**, 384 (1932)].

[5] Pickard and Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); **101**, 620 (1912); **105**, 830 (1914); **105**, 1115 (1914).

[6] Levene and Marker, *J. Biol. Chem.*, **90**, 669 (1931).

[7] Levene and Marker, *ibid.*, **92**, 379 (1932).

[8] See Freudenberg, "Stereochemie," 1932, p. 696.

[9] These carbinols were correlated by the Displacement Rule, Freudenberg, *Sitzber. Heidelberg Akad. Wiss.*, 1931, 9 Abh.

Above is assembled a series of carbinols showing the effect of the branched chain on optical activity. With the exception of the phenyl group, the isopropyl group causes the greatest depression of the optical activity, the cyclohexyl next and lastly the tertiary-butyl group, while the isobutyl group causes an exaltation.[10] The unexpected fact that the isopropyl group causes a greater shift than the tertiary-butyl group may be due to the presence in the former of a tertiary hydrogen atom. Furthermore, it is not impossible that the depression of the optical rotation in the case of methyl-tertiarybutylcarbinol may be illusory, due to incomplete resolution. A determination of the configuration and maximum rotation of the next higher member of this series, ethyl-tertiary-butylcarbinol, would indicate whether a shift really exists or not. Work in this direction is now in progress.

I wish to express my thanks to Professor James F. Norris for the use of the facilities of this Laboratory. Part of the funds required for this research were privately contributed.

Experimental

In this work all rotations are dextro and for the homogeneous state unless otherwise designated.

Dextro Methylisopropylcarbinol Acetate.—8.8 g. of the carbinol was treated with 12.3 g. of acetic anhydride and 15 cc. of dry pyridine. After standing overnight at 25°, the mixture was warmed on the steam-bath for two hours, shaken with ice, ether and dilute sulfuric acid, then with dilute sodium hydroxide, dried over anhydrous potassium carbonate and fractionated through a 61-cm. adiabatic controlled reflux column.

1st fraction	b. p. (758 mm.) 124–128.2°		2.7 g.	93% yield
2nd fraction	b. p. (758 mm.) 128.2–128.9°	α^{25}_{D} 3.64°	6.1 g.	
Residue			3.3 g.	

The second fraction was redistilled.

Dextro Methylisopropylcarbinol Benzoate.—6.0 g. of the carbinol dissolved in 15 cc. of dry pyridine was treated in the cold with 8.6 cc. (10.4 g.) of redistilled benzoyl chloride. The mixture after standing overnight at 25° was worked up as was the acetate, and distilled, b. p. (2 mm.) 80.5–81.0° (bath 105°), yield 9.2 g., α^{26}_{D} 9.26°. This material was redistilled, b. p. (2 mm.) 83–84° (bath 120°). The benzoate was colorless, almost odorless and contained no halogen by the Beilstein test.

Dextro Methyl-tertiary-butylcarbinol.—The carbinol, b. p. (764 mm.) 118–121°, prepared from tertiary-butylmagnesium chloride and acetaldehyde, was converted into the acid phthalate with phthalic anhydride and pyridine, and then resolved with brucine in acetone solution. Five recrystallizations of the salt were sufficient. The carbinol was recovered in the usual way and fractionated.

Dextro Methyl-tertiary-butylcarbinol Acetate.—9.0 g. of the carbinol was treated with 10.0 g. of acetic anhydride and 15 cc. of dry pyridine exactly as described for methylisopropylcarbinol acetate. The acetate was fractionated.

First fraction (756 mm.) 135–140.5°
Second fraction (756 mm.) 140.5–141.0° α^{27}_{D} 9.46°

The second fraction was redistilled.

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[10] Similar relations hold in the hydrocarbon series, Levene and Marker, *J. Biol. Chem.*, **91**, 405 (1931); **95**, 1 (1932); **100**, 685 (1933).

SUMMARY OF PHYSICAL CONSTANTS AT 25°

	Methyl-isopropyl	α 589	α 546	α 472	472/589	d_4	n_D	B. p. °C.	B. p. Mm.
1	Carbinol	0.90	1.07	1.45	1.611	0.810	....	....	...
2	Acetate	3.68	4.31	5.91	1.606	.860	1.3932	128.5–129	758
3	Benzoate	9.27[a]	10.98[a]	15.28[a]	1.648	.979	1.4887	....	...
	Methyl-*t*-butyl								
4	Carbinol	3.78[b]	4.50[b]	6.33[b]	1.675	.810	....	120.0	760
5	Acetate	9.63	11.28	15.33	1.592	.856	1.4001	141.0[13]	756
6	Benzoate	27.92[a]	33.03[a]	46.00[a]	1.647	.970	1.4882	105–105.5	5

	$[M]_D$	Max. $[M]_D$	Max. conv. factor	$[\alpha]_D$ ($CHCl_3$)	Max. $[M]_D$ ($CHCl_3$)	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
1	0.979	4.296[11]	4.39	....	..	......	..	..	..	..
2	5.60	24.6	...	....	..	$C_7H_{14}O_2$	64.6	64.5	10.8	10.9
3	18.18[a]	79.8	...	8.81[a]	74.3	$C_{12}H_{16}O_2$	75.0	75.2	8.4	8.2
4	4.86	7.65[12]	1.574	....	..	......	..	..	..	..
5	16.21	25.5	...	....	..	$C_8H_{16}O_2$	66.6	66.0	11.2	11.2
6	59.32	93.4	...	26.61[a]	86.3	$C_{13}H_{18}O_2$	75.7	75.7	8.8	8.9

[a] At 26°. [b] At 27°.

Dextro Methyl-tertiary-butylcarbinol Benzoate.—The benzoate was prepared as described for methylisopropylcarbinol benzoate, 6.0 g. of the carbinol yielding 8.4 g. of pure benzoate, b. p. (5 mm.) 105.0–106° (bath 138°), α_D^{26} 27.92°. This material was redistilled.

Summary

1. Dextro methyl-tertiary-butylcarbinol is configurationally related, according to the Displacement Rule of Freudenberg, to dextro methyl-*n*-butylcarbinol.

2. The tertiary-butyl group lowers the optical rotation, but not as much as the isopropyl group or the cyclohexyl group.

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(11) Calculated from Pickard and Kenyon's data, *J. Chem. Soc.*, **101**, 637 (1912).

(12) Calculated from data of Pickard and Kenyon, *ibid.*, **105**, 1121 (1914).

(13) Compare Whitmore and Rothrock, THIS JOURNAL, **55**, 1106 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Action of Bromine on Acetomesitylene. Polyhalo Derivatives of 3,5-Dibromoacetylmesitylene[1]

BY C. HAROLD FISHER

Several attempts to prepare α-tribromoacetophenones by direct bromination of the corresponding acetophenones have been reported unsuccessful.[2] However, by working in the absence of solvent, Adams[3] was able to introduce three bromine atoms into the acetyl group of bromopaeonol (2-hydroxy-4-methoxy-5-bromoacetophenone). In view of this fact, and the ease with which the ring of mesitylene derivatives has been brominated,[4] it seemed likely that liquid bromine would convert acetomesitylene into α,α,α,3,5-pentabromoacetylmesitylene (I). It was found that actually a mixture of polybromoacetylmesitylenes melting at 102–108° was formed, which on fractional crystallization yielded the expected pentabromo compound (m. p. 113–114°) and a substance melting at 108–109°. The action of liquid bromine on α,α,α-tribromoacetylmesitylene[5] gave precisely the same results.

Attempts were made to transform the pentabromo compound (I) into 3,5-dibromo-β-isodurylic acid (II) by alkaline cleavage as a method of structure determination. However, this cleavage, which would hardly be expected in view of the difficulty experienced in the cleavage of similarly hindered α-tribromoacetophenones, could not be accomplished. Accordingly, it was planned to synthesize α,α,α,3,5-pentabromoacetylmesitylene (I) by a method[6] which has been shown to be generally applicable to hindered acetophenones. The compound, 3,5-dibromoacetylmesitylene (IV), needed as a starting point in this synthesis was prepared by reducing with zinc and acetic acid[7] the crude product, described above, prepared by brominating acetomesitylene without a solvent. Although the material reduced was a mixture, only one reduction product (IV) was obtained. The bromine content (two atoms) and method of preparation appeared to exclude all structures except that of 3,5-dibromoacetylmesitylene (IV), but confirmation was arrived at by its conversion, in two steps, into 3,5-dibromo-β-isodurylic acid (II).

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(1) A portion of this work was carried out with Professor Reynold C. Fuson (Dissertation, University of Illinois, 1932), to whom the author wishes to express his thanks for the kind permission to continue the work elsewhere.

(2) Hunnius, *Ber.*, **10**, 2010 (1877); Engler and Zielke, *ibid.*, **22**, 204 (1889); Gabriel and Michael, *ibid.*, **11**, 1007 (1878).

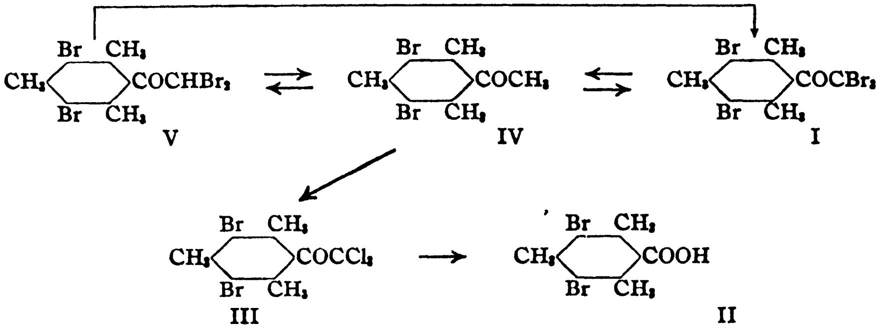
(3) Adams, THIS JOURNAL, **41**, 262 (1919).

(4) Shildneck and Adams, *ibid.*, **53**, 351 (1931).

(5) Fuson and Walker, *ibid.*, **52**, 3269 (1930).

(6) One of the recent papers in this series: Fuson, Bertetti and Ross, *ibid.*, **54**, 4380 (1932).

(7) This reduction method was shown to be applicable to tribromoacetophenones by its use in the case of a previously-described compound, tribromoacetylmesitylene.[5] The product, acetomesitylene, was identified by conversion into its solid nitration product.[8]



The action of sodium hypochlorite caused the formation of α,α,α-trichloro-3,5-dibromoacetylmesitylene (III), which was then cleaved by the action of hot alkali to the dibromo acid (II). This acid was identical with a sample of 3,5-dibromo-β-isodurylic acid prepared according to the directions of Shildneck and Adams.[4]

The preparation of α,α,α,3,5-pentabromoacetylmesitylene (I) was brought about by treating 3,5-dibromoacetylmesitylene (IV) with a solution of sodium hypobromite. The product thus formed was identical with the pentabromo compound (m. p. 113–114°) previously obtained by the bromination of acetomesitylene. The pentabromo ketone (I) was produced also, but in a less pure state, when the mixture obtained by the action of liquid bromine on acetomesitylene was treated with sodium hypobromite.

The other substance (m. p. 108–109°) obtained by the action of liquid bromine on acetomesitylene was prepared by treating an acetic acid solution of 3,5-dibromoacetylmesitylene (IV) with an excess of bromine, and was shown to be composed of the pentabromo ketone (I) and α,α,3,5-tetrabromoacetylmesitylene (V). The evidence supporting this conclusion is as follows: analyses showed the presence of four and one-half bromine atoms, and molecular weight determinations gave a value midway between the molecular weights of tetrabromo- and pentabromoacetylmesitylene. The same product, m. p. 108–109°, was obtained when equimolar quantities of α,α,3,5-tetrabromoacetylmesitylene (V) (prepared by treating an acetic acid solution of 3,5-dibromoacetylmesitylene (IV) with two moles of bromine) and pentabromoacetylmesitylene (I) were crystallized together. Reduction of the product melting at 108–109° with zinc and acetic acid gave the dibromo ketone (IV), and the action of sodium hypobromite caused the formation of the pentabromo ketone (I). The same substance (m. p. 108–109°) was synthesized by the action of bromine on an acetic acid solution of α,α,3,5-tetrabromoacetylmesitylene (V), and in another case by the action of an acetic acid solution of bromine and hydrogen bromide on the pentabromo ketone (I). The substance, m. p. 108–109°, behaved toward cold alkali[8] as would be expected: the dibromomethyl ketone was converted into an alkali-soluble product, leaving undissolved the pentabromo ketone (I).

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[8] Engler and Wöhrle, *Ber.*, **20**, 2201 (1887).

The kind and helpful suggestions of Professor Louis F. Fieser are gratefully acknowledged.

Experimental

The Action of Bromine on Acetomesitylene and α,α,α-Tribromoacetylmesitylene.[5]—In each case an excess (5 to 9 parts by weight to one of ketone) of previously-cooled bromine was added slowly to the organic compound contained in a flask surrounded by an ice-bath. After the reaction had become less vigorous the ice-bath was removed, and the reaction mixture allowed to stand four hours with occasional shaking at room temperature. Most of the excess bromine was removed with a stream of air. A cold solution of sodium bisulfite was added and the mixture filtered. Fractional crystallization in alcohol of the residue, a nearly colorless solid, yielded two substances which melted at 108–109° and 113–114°. A larger quantity of the higher melting compound was usually obtained. It was found possible to prepare both products in a high state of purity and more conveniently by other methods described below.

3,5-Dibromoacetylmesitylene (IV).—Reduction with zinc dust and acetic acid caused the replacement of all the bromine atoms of the acetyl group with hydrogen atoms in the case of α,α,α-tribromoacetylmesitylene, pentabromoacetylmesitylene (I), tetrabromoacetylmesitylene (V) and the product (m. p. 108–109°) consisting of the tetra- and pentabromoacetylmesitylenes (V and I). Each ketone (6 g.) was heated for four hours on a steam cone with 12 g. of zinc dust and 60 cc. of acetic acid. The reaction mixture was filtered and the residue washed with hot acetic acid. The combined filtrates were concentrated and added to water. The solid which precipitated crystallized in alcohol as colorless leaflets or cubes, m. p. 147.5–148.5°. The yields were good.

Anal. Calcd. for $C_{11}H_{12}OBr_2$: Br, 50.0. Found: Br, 50.4.

α,α,α-Tribromoacetylmesitylene gave an oil which yielded a nitration product identical with the substance[5] previously prepared by nitrating acetomesitylene.

α,α,α-Trichloro-3,5-dibromoacetylmesitylene (III).—A solution of 2 g. of 3,5-dibromoacetylmesitylene in 100 cc. of pyridine was added to 100 cc. of a sodium hypochlorite solution, which had been prepared[6] from a 10% sodium hydroxide solution. The resulting mixture was agitated for several days. The product was filtered, washed with water, and crystallized from alcohol, giving colorless needles which melted at 102–103°.

Anal. Calcd. for $C_{11}H_9OCl_3Br_2$: C, 31.2; H, 2.1. Found: C, 31.1; H, 2.1.

3,5-Dibromo-β-isodurylic Acid (II).—A small amount of the dibromo acid was obtained by heating 1.9 g. of α,α,α-trichloro-3,5-dibromoacetylmesitylene with 10 g. of sodium hydroxide, 10 cc. of water and 20 cc. of dioxane on a steam cone for twelve hours, and then two hours (refluxing) over a flame. Most of the starting material was recovered unchanged.

A good yield of the acid was obtained by refluxing for five hours a mixture of 1.5 g. of the trichloro ketone, 10 g. of sodium hydroxide, 15 cc. of water and 5 cc. of methyl alcohol. The sodium salt of the acid was washed with ether, dissolved in hot water (the sodium salt is comparatively insoluble in cold water) and filtered. The precipitate obtained by acidification with hydrochloric acid was crystallized from a methanol-water solution, and found to be identical (mixed melting point) with an authentic sample of 3,5-dibromo-β-isodurylic acid.[4]

Brominations with Sodium Hypobromite.—3,5-Dibromoacetylmesitylene (IV), α,α,3,5-tetrabromoacetylmesitylene (V) and the sharply-melting (108–109°) mixture (VI) of the tetra- and pentabromoacetylmesitylenes (V and I) were converted into the pentabromo ketone (I). The data are given below.

Ketone, g.	Pyridine, cc.	Water, cc.	Sodium hydroxide, g.	Bromine, cc.	Time of stirring, hrs.	M. p., °C.	Yield, g.
IV, 1	25	275	30	9.5	48	112–113.5	1
V, 1.5	25	300	30	9.5	67	112.5–113.5	1.3
VI, 1.5	50	250	30	9.5	48	112.5–113.5	1.3

The proportions of pyridine and water used in the last-mentioned preparation caused the formation of two layers. After several crystallizations from alcohol the product was obtained as large, colorless needles melting at 113–114°.

Anal. Calcd. for $C_{11}H_9OBr_5$: C, 23.7; H, 1.6; mol. wt., 557. Found: C, 23.8; H, 1.7; mol. wt. (cryoscopic in benzene), 539.

The Action of an Excess of Bromine on 3,5-Dibromoacetylmesitylene in Acetic Acid.—A solution of 8 g. (0.025 mole) of the dibromo ketone in 100 cc. of glacial acetic acid was stirred mechanically, and heated in a boiling water-bath, and 12 g. (0.075 mole) of bromine was added from a dropping funnel in the course of ten minutes. After stirring and heating had continued for one and one-half hours, the dropping funnel was replaced by a glass tube extending below the surface of the solution, and for one and three-quarters hours air was drawn through this tube by means of a water pump connected to the top of the condenser (heating and stirring). The solution on cooling deposited 9.8 g. of needles melting at 107.5–109°. After repeated crystallization from alcohol the product melted at 108–109°, and was found to be identical with the substance (m. p. 108–109°) obtained by the action of bromine, without solvent, on acetomesitylene. The bromination of α,α,3,5-tetrabromoacetylmesitylene under these conditions gave the same result.

Anal. Calcd. for $C_{11}H_{10}OBr_4{\cdot}C_{11}H_9OBr_5$: C, 25.5; H, 1.9; mol. wt., 518. Found: C, 25.8, 25.5; H, 2.0, 2.0; mol. wt. (cryoscopic in benzene), 516, 513.

A preparation carried out later with different quantities (11 g. (0.034 mole) of dibromo ketone, 22.4 g. (0.14 mole) of bromine, 110 cc. of acetic acid) was found to yield a mixture (separated by fractional crystallization) of the usual product (m. p. 108–109°) and α,α,α,3,5-pentabromoacetylmesitylene.

The Crystallization of a Mixture of Tetrabromoacetylmesitylene (V) and Pentabromoacetylmesitylene (I).—A mixture of the pentabromo (0.56 g.) and tetrabromo (0.48 g.) ketones was crystallized from alcohol. The product (0.9 g.) melted at 108–109°, and was identical with the product, m. p. 108–109°, obtained by the action of an excess of bromine on 3,5-dibromoacetylmesitylene in acetic acid. The melting point was not altered by six additional crystallizations from alcohol.

α,α,3,5-Tetrabromoacetylmesitylene (V).—This compound was prepared in good yield by adding 2 moles of bromine to an acetic acid solution of 3,5-dibromoacetylmesitylene, which was mechanically stirred and heated by a water-bath. The product crystallized from alcohol as colorless needles melting at 143–144°.

Anal. Calcd. for $C_{11}H_{10}OBr_4$: Br, 66.9. Found: Br, 66.8.

The Action of Bromine and Hydrogen Bromide on α,α,α,3,5-Pentabromoacetylmesitylene.—A solution of 0.56 g. of pentabromoacetylmesitylene, 10 cc. of acetic acid, 10 drops of 48% hydrobromic acid and 5 drops of bromine was heated with mechanical stirring in a three-necked flask on a water-bath for half an hour. Five drops of bromine was then added, and the stirring continued one hour. The needles (0.30 g.) which formed when the reaction solution cooled melted at 108–109°, and was identical with the sharply-melting (108–109°) substance previously obtained by treating an acetic acid solution of 3,5-dibromoacetylmesitylene with an excess of bromine. More of the same product (m. p. 107.5–109°) was precipitated by adding water to the mother liquor.

α,α,α,3,5-Pentabromoacetylmesitylene (I). (By Use of Potassium Hydroxide.)—

One gram of the sharply-melting (108–109°) product obtained by treating an acetic acid solution of 3,5-dibromoacetylmesitylene with an excess of bromine was pulverized in an agate mortar and shaken mechanically with 50 cc. of a 10% potassium hydroxide solution for twenty-four hours. Acidification of the reaction mixture (after washing with ether) gave a precipitate in insufficient amount for identification. Evaporation of the ether left a residue, from which the pentabromo ketone, melting at 112–113°, was isolated by extraction with hot alcohol. A small amount of a substance sparingly soluble in hot alcohol, and very soluble in benzene, was isolated but not identified.

Summary

It has been shown that bromine reacts in the absence of solvent with acetomesitylene to give a tribromomethyl ketone and a sharply-melting substance consisting of the same tribromomethyl ketone and the corresponding dibromomethyl ketone. Bromine in acetic acid was less efficient in halogenating the acetyl group since the chief product was the sharply-melting mixture of the dibromo- and tribromo-methyl ketones.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. IV. The Dehydrogenation of Paraffin Hydrocarbons and the Strength of the C–C Bond

BY F. O. RICE AND M. DENISE DOOLEY

The thermal decomposition of ethane has been studied recently in two papers,[1] and it has been concluded that the only reaction occurring to an appreciable extent is the simple dehydrogenation to C_2H_4; the reaction is homogeneous and unimolecular, with an activation energy of about 73 cal. It would seem from this that the decomposition of ethane can best be represented as the separation of molecular hydrogen from the ethane molecule with the formation of a double bond between the two carbon atoms to give ethylene. This view has received further support from the work of Pease,[2] who has shown that the formation of ethane from ethylene and hydrogen is a second order reaction with an energy of activation of 43,150 cal. The heat of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ at room temperature and constant pressure is 30,600 cal.[3] and at 600–700° and constant volume is 31,244 cal.[4] The activation energy of the reaction $C_2H_6 \longrightarrow C_2H_4 + H_2$ is therefore $43{,}150 + 31{,}244 = 74{,}394$ cal., a figure which is in excellent agreement with the experimental value of 73,170 cal. obtained by Marek and McCluer.[1]

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(1) Frey and Smith, *Ind. Eng. Chem.*, **20**, 948 (1928); Marek and McCluer, *ibid.*, **23**, 878 (1931).

(2) Pease, THIS JOURNAL, **54**, 1878 (1932).

(3) Von Wartenberg and Krause, *Z. physik. Chem.*, **151**, 105 (1930).

(4) Pease and Durgan, THIS JOURNAL, **50**, 2715 (1928).

One might expect from this that the dehydrogenation, not only of ethane but also of its homologs, can best be represented as the separation of molecular hydrogen with the formation of the corresponding olefin hydrocarbon. Now if this simple process really takes place, it seems reasonable to suppose that there would be some fairly obvious relation between the structure of a hydrocarbon and the extent of the dehydrogenation process. The experimental results for several hydrocarbons are given in Fig. 1 (heavy line);[5] an inspection of these shows that the structure of the hydrocarbon gives no clue as to the extent to which dehydrogenation takes place; thus propane gives 23% hydrogen in the products but *n*-butane only 4.5%; isobutane gives 26.4% which cannot be due to a tertiary hydrogen atom because 2,3-dimethylbutene gives only 3% hydrogen.

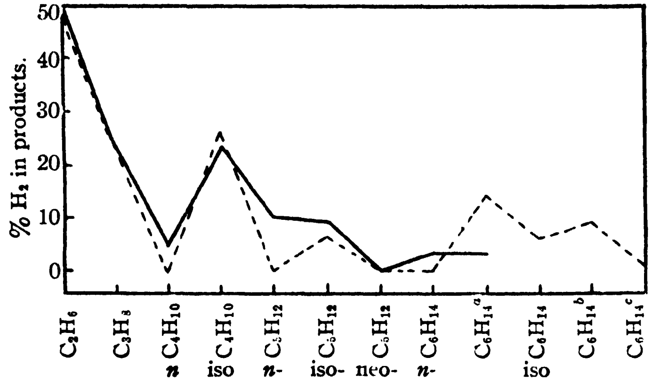

Fig. 1.—Observed (—) and calculated (- - -) hydrogen production in the thermal decomposition of hydrocarbons. [a] 2,3-Dimethylbutane. [b] 2,2-Dimethylbutane. [c] 3-Ethylpentane.

When, however, we consider the decomposition from the standpoint of free radicals,[6] the agreement is much better; the calculated results are shown in Fig. 1 (dotted line).

It occurred to us that it is possible to make an experimental test of these two mechanisms by decomposing ethane according to a method already described[7] and testing for the presence of free radicals by the Paneth effect[8] on metallic mirrors. Ethylene[9] has no effect on a metallic mirror when heated under these conditions, and we confirmed the original observation of Paneth and Hofeditz[8] that hydrogen also has no effect. Therefore, if ethane decomposes according to the equation $C_2H_6 \longrightarrow C_2H_4 + H_2$, there should be no removal of a metallic mirror; whereas, if it decomposes according to the equation $C_2H_6 \longrightarrow 2CH_3$, mirrors should be readily removed.

(5) Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933).

(6) Rice, This Journal, **53**, 1959 (1931); **55**, 3035 (1933).

(7) Rice, Evering and Johnston, *ibid.*, **54**, 3529 (1932).

(8) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(9) Fred R. Whaley, Ph.D. Thesis, 1932, Johns Hopkins University.

A preliminary test with ordinary commercial ethane (90%) showed rapid removal in the range 850–950°. However, in order to determine that the effect was not due to small amounts of impurities (such as propane), we prepared a sample of ethane by the Grignard reaction, using methylmagnesium bromide, and removed ether and other impurities by passing through a trap at −80° and distilling through a vacuum jacketed column. This sample and the commercial sample gave identical results. We concluded therefore that the reaction $C_2H_6 \longrightarrow 2CH_3$ takes place at any rate to some extent in the range 850–950°.

Our next step was to measure the activation energy of this reaction[10] by depositing standard mirrors of antimony on the walls of the tube at different distances from the furnace. In this manner we obtained a relative measure of the concentration of radicals at the end of the furnace at measured furnace temperatures. We performed a number of experiments using in each case commercial ethane which had been distilled through a vacuum jacketed column. In one series of experiments at 960 and 906° using a quartz tube 1.3 cm. in diameter and a furnace 15 cm. long we obtained the following results

Dist. from end of furnace, cm.	2.5	2.1	1.5	1.0	0.7
Ratio t_{906}/t_{960}	3.14	3.31	3.73	3.88	4.08
Activation energy	61,600	64,500	71,000	73,000	76,000

The ratio t_{906}/t_{960} is the ratio of the times of disappearance of two standard mirrors for these two furnace temperatures; the extrapolated value for the end of the furnace is 4.44, which corresponds to an activation energy of 80,000 cal. The mean value of three such experiments with ethane is 79,500 ± 3000 cal. In order to test the apparatus we performed a similar experiment using acetone at furnace temperatures 742 and 795° and obtained an activation energy of 69,000 cal. which is also in good agreement with a previous result.

Summary

We have shown that when ethane is heated in the range 850–950° free radicals are present. Furthermore, we have shown that the activation energy of the dissociation of ethane into methyl groups is very close to the measured activation energy of ethane. Accordingly, either the formation of ethylene and hydrogen from ethane goes through a free radical mechanism, or the free radical mechanism and a simple separation of hydrogen occur simultaneously. The value 79,500 cal. for the dissociation of ethane into two methyl groups plus the average energy (about 5000 cal.) gives an upper limit for the strength of the C–C bond.

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[10] See Ref. 7, p. 3540.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Potato Starch[1]

BY T. C. TAYLOR AND T. J. SCHOCH

In the cereal starches such as corn, wheat and rice, there is a certain amount of material which cannot be dissociated and subsequently dispersed to give a clear solution in any amount of water. This is called α amylose[2] or amylopectin and carries with it combined fatty acids.[3] Whether potato starch which has no appreciable amount of combined fatty material contains any of this insoluble α amylose or is all soluble beta amylose is a moot question.

Potato starch does carry, however, combined with it phosphate radicals, but where they are and how they contribute to the properties of the potato starch is also an open question despite considerable work. Some think the phosphorus is attached to one amylose and not to others[4] and some think that it is distributed throughout.[5]

In line with the attempts which have been made in the laboratory to define more rigorously the starches and their amyloses, potato starch has been carefully studied because many modern interpretations of starch structure are dependent upon data of this kind. This is a report of such a study.

It scarcely need be recalled that all attempts to gain information concerning the amyloses, involves some sort of disorganization of the starch granules. This break-up should be brought about without chemical change but it has been difficult in the past to do other than express the hope that no change had taken place during dissociation, since there have existed no sufficiently sensitive tests by which to detect chemical alteration.

Previous investigations[6] on potato starch have placed considerable significance on the phosphorus content of various alleged amyloses. It will be shown, however, that it is almost impossible to rely on these findings in attempting to delineate any distinct potato starch amyloses.

In this work various methods of disorganization of the granule have been studied and correlated with phosphorus content of the recovered amyloid material, ease of retrogradation[7] and chemical alteration as measured by the

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(1) An abstract of a dissertation presented by T. J. Schoch to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Meyer, "Die Starkekörne," Jena, 1895.

(3) (a) Taylor and Nelson, THIS JOURNAL, **42**, 1726 (1920); (b) Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

(4) (a) Samec, *Kolloidchem. Beihefte*, **4**, 132 (1912); **5**, 141 (1913); **6**, 23 (1914); **8**, 33 (1916); (b) Baldwin, THIS JOURNAL, **52**, 2907 (1930).

(5) Karrer, *Helv. Chim. Acta*, **12**, 1144 (1929); **15**, 48 (1932).

(6) (a) Malfitano and Catoire, *Compt. rend.*, **177**, 1309 (1923); (b) see 4 (b); (c) Sherman and Baker, THIS JOURNAL, **38**, 1885 (1916).

(7) Walton, "A Comprehensive Survey of Starch Chemistry," The Chemical Catalog Co., New York, 1923, p. 135.

recent alkali labile method of Taylor and Salzmann[8] all with a view toward finding and defining the amylose or amyloses in potato starch.

I. A repetition of the ammonium thiocyanate gelatinization and electrophoretic separation technique of Taylor and Iddles with slight modifications, gave an insoluble migratable residue of approximately 3.5% containing 0.036% phosphorus and a soluble fraction containing 0.060% phosphorus. The original potato starch phosphorus content was 0.069%.

Since any insoluble material resulting from an attempted fractionation is commonly designated amylopectin (α amylose), potato starch would be considered to have about 3.6% of this fraction. Contrary to Samec's[4a] findings and the results of the work of Baldwin,[4b] the phosphorus is mainly in the soluble portion under these conditions, the insoluble material which migrates here having only half the original phosphorus content. Later, it will be shown that under other conditions insoluble residues may be found that are high in phosphorus. No inorganic phosphate is likely to be the cause of this discrepancy since the experiment is carried out under conditions that bring about a forced dialysis of electrolyte away from the amyloid material. Experiments on additions of known amounts of secondary potassium phosphate to the cells during the course of the separation showed that it was quantitatively removed to the level of the original organic (non-dialyzable) phosphorus. So the distribution of the phosphorus in what appears to be amylose fractions in the above experiments is not due to a partitioning of extraneous phosphate ions. Since the presence of thiocyanate ions prevents retrogradation, this insoluble residue probably comes from organized starchy material. Furthermore, the electrical mobility of the insoluble fraction turns out to be due apparently to the presence of adsorbed thiocyanate ion for when this is removed by long extraction of the sample with alcohol the same amount of suspension containing identically the same amount of phosphorus as in the previous case does not migrate even under a difference of potential of 1200 volts over long periods of time.

II. Instead of disorganization by gelatinization with a swelling agent, samples of potato starch were dry ground in a pebble mill[9] and then dispersed in boiling water. As has been noticed frequently, previously clear dispersions of potato starch rapidly become cloudy and deposit on standing the bulk of their solid material in an insoluble form. This is "retrogradation or reversion"[7] and the material so deposited cannot be redispersed successfully. In this instance, the clear 15% dispersions made in boiling water reverted on standing unless the pre-grinding of the starch had approximated five hundred hours when it was possible to examine the solutions without development of excessive cloudiness even during relatively long periods of time.

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(8) Taylor and Salzmann, THIS JOURNAL, **55**, 264 (1933).

(9) (a) Alsberg and Perry, *J. Biol. Chem.*, **63**, 66 (1925); (b) Taylor and Beckmann, THIS JOURNAL, **51**, 294 (1929).

In the electrophoretic cell[8b] there was no migration of the cloudy material from incipient retrogradation over a period of four months under 1200 volts d. c., the solution being protected from molds by toluene

Suction filtration of another sample of this 5% dispersion through especially prepared collodion membranes (see Experimental section) on a modified Buchner funnel gave no residue other than a little silica. The clear filtrate was electro-dialyzed[10] against running water for several days, and the solids precipitated from it by the addition of alcohol. Practically the entire amount of starch could be accounted for in this filtrate and substantially all the phosphorus of the original starch was present as combined phosphate in the solid precipitated from the clear filtrate by alcohol. (Original starch P% 0.070, 0.077 and 0.069. Alcohol precipitated amylose from filtrate P% 0.078, 0.076 and 0.071.) These findings are contrary again to those of Samec[4] and others, who find little or no phosphorus in the soluble material from potato starch.

If the dry starch is ground for shorter periods of time, the dispersion in hot water reverts so quickly that large quantities of potentially soluble material become insoluble and the fraction of alleged amylopectin is increased. For example, a 5% paste made from potato starch ground for one hundred twenty hours will in the course of a few days deposit substantially all of its previously soluble material as an insoluble mass. The insoluble material deposited during retrogradation contains the same amount of phosphorus as the original starch from which it came. This may explain Samec's observations that the insoluble material (false amylopectin[11]) contains such a large amount of phosphorus.

Unless the solubilizing effect of grinding is accompanied by no chemical changes, the results are, of course, open to doubt. One criterion is the determination of the alkali labile[8] portion or its complement, the alkali stable portion, of a starch after a given treatment. Such a determination shows that in a raw potato starch of good quality 98% is stable to the effect of hot aqueous alkali, while after one hundred twenty hours grinding 78% is unchanged and after five hundred hours 55% is unchanged. Since some change is indicated, in the samples used here, the disorganization by the pebble mill is not above suspicion.

III. Mechanical disintegration of swollen granules in a water paste in a homogenizer[9b] was not successful in the past in completely disorganizing the starch but it was tried again here in a totally different type of mill[12] but was still not completely successful. While something was accomplished in reducing the paste viscosity,[9b] which is a rough measure of the progress of disorganization, there were still many micromolecular clots

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(10) A cell as used by Taylor and Iddles (see Ref. 3 (b)) may be used when provision is made for passing tap water through the two outside electrode compartments.

(11) Reychler, *Bull. soc. chim. Belg. Grand*, **29**, 309 (1920).

(12) See Experimental section.

present. This paste was nevertheless placed in the electrophoretic cell and the potential applied. The gross insoluble material migrated to the anode leaving a clear supernatant liquid containing only about 20% of the weight of the original starch. Soluble material was precipitated with alcohol and analyzed. It contained 0.003% phosphorus (dry basis) and 93% of starch material was stable to alkali.

After several trials with a more viscous suspending medium, including mineral oil and several concentrations of glycerin, a 5% potato starch paste was made in 85% glycerin by repeatedly passing the cooled mixture through the colloid mill. From the paste the solids were precipitated by the addition of an excess of alcohol, giving a material which will *completely* redisperse but which retrogrades readily. A newly prepared solution will pass in its entirety through a collodion ultrafilter. The filtrate after forced dialysis against water gave a residue on precipitation with alcohol, 93% of which was stable toward alkali[8] and which contained 0.065% phosphorus.

It is evident that the amyloid material in potato starch may be completely dispersed to give clear solutions *without alteration* as measured by the action of aqueous alkali and that, despite its solubility, it contains substantially all the organic phosphate radicals.

IV. Contrasted with the foregoing methods are those in which a starch paste is made by partial gelatinization at 63 and at 85°, and the swollen material frozen, then thawed and any surviving soluble material recovered by filtration. Repeating this old technique as modified by Baldwin,[4b] 17% of the original starch was recovered, containing 0.019% phosphorus. The material, it would seem, represents the small fraction of the total ultimately available soluble material in potato starch, released from a few granules that have disintegrated or partially leached from others; which soluble material fortuitously has not undergone retrogradation. If the residue from the filtration is gently ground with sand, a further amount of material becomes soluble. In the cold, any of this soluble material is to a large extent irreversibly precipitated from water solution, that is, it undergoes retrogradation to a fibrous mass.[13]

Hirst, Plant and Wilkinson[14] also have recently reported that by maintaining potato starch pastes at −10 to −15° overnight, soluble amylose may be readily filtered from the insoluble residue. Quoting in part from this report, "The material which remained after long extraction of the fibrous mass with hot water was considered to be amylopectin," *i. e.*, alpha-amylose. In this investigation, freezing temperatures over a period of several days have been shown to result in more than 95% retrogradation of the soluble amylose derived from the original raw starch.

Incidentally, Hirst finds no chemical differences between the soluble and the insoluble material from potato starch with regard to yield of methylated glucoses and therefore glucose anhydride chain length.[14,15]

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[13] Scharling, *Ann.*, **49**, 315 (1844).

[14] Hirst, Plant and Wilkinson, *J. Chem. Soc.*, 2375 (1932).

Thus far, all evidence points to the presence of a soluble phase, only, in potato starch providing care is exercised to avoid such complicating factors as retrogradation or incomplete disorganization of the granule. It is also obvious that the amount of phosphorus combined with the carbohydrate varies over wide limits in various fractions, no matter how obtained, and irrespective of solubility, a finding in accord with the observations of Karrer.[5]

To explain these observations, there is the hypothesis that chains of glucose anhydrides make up the amylose unit and that aggregations of these make the micelli which are in turn arranged in microscopic geometrical packages called granules. It is possible to use the postulates of Meyer and Mark[16] concerning the presence of more or less completely esterified tribasic phosphoric acid, either with hydroxyl groups on one chain or bridging between two chains of glucose anhydrides. These chains may vary over a wide range with regard to the amount of phosphate held to them, giving rise to a kind of heterogeneity even though all these fractions unlike those from the cereal starches are soluble.

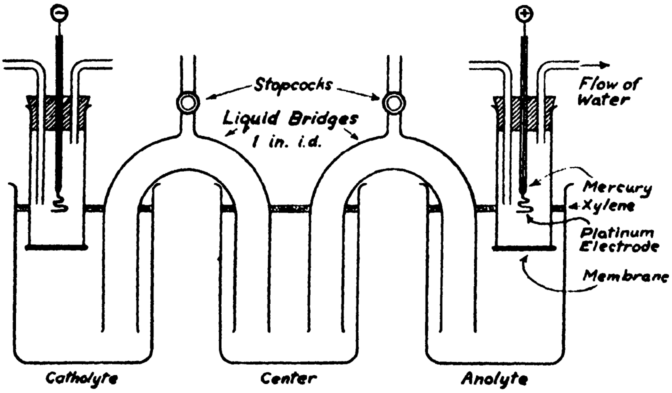

Fig. 1.

To test this experimentally on the supposition that the electrical mobility of certain of the soluble fractions might be different from others due to variation in the ratio of phosphorus to carbohydrate and possibly to the degree of esterification and therefore admit of a qualitative separation, a technique similar to that used for the determination of transport number was employed (see Fig. 1). The results are given in Table I.

Run (1) 4% clear hot-water dispersion of 500-hr. dry ground starch. Time of treatment in cell, five days.

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(15) Haworth and Percival, *J. Chem. Soc.*, 2278–2279 (1932).

(16) Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Leipzig, 1930.

TABLE I

Results in runs of same number are to be compared

Electrode compartment	Run[a]	Dry wt., %	Phosphorus, %		Alkali labile mg.[a] iodine per 100 mg. sample	
	1	3.8	0.041	0.052	23.8	..
Anode	2	4.0	.081	..	23.6	..
	3	1.5	.079	...	4.4	..
	1	4.0	.043	...	28.0	..
Center	2	4.0	.047	0.058	26.7	..
	3	1.4	.075	...	5.0	..
	1	3.9	.017	...	27.9	27.7
Cathode	2	4.1	.024	0.029	27.4	27.3
	3	0.3	.012	...	5.3	..

[a] It is interesting to note that Fernbach [*Compt. rend.*, **138**, 428 (1904)] observed that the smaller granules of potato starch contained more phosphorus than the larger ones.

Run (2) 4% clear hot-water dispersion of 500-hr. dry ground starch. Time of treatment in cell, twelve days.

Run (3) test run on 1% simple hot water gelatinized cloudy suspension of whole starch. Time of treatment, ten days.

Original starch P% 0.074.

Dry weight was estimated semi-quantitatively by the addition of a large excess of alcohol, followed by filtration, drying and weighing.

Alkali lability was here determined iodimetrically since the alcohol precipitation method is not sufficiently precise to disclose minor deviations. Minimum excesses of iodine and of alkali, as predetermined in each case by rough titration, were employed to avoid over-oxidation.

In each instance there has occurred a migration of the high phosphorus-bearing amylose toward the anode, apparently with a compensating counter-flow of material low in phosphorus. It will be noticed that there is a gradation in alkali lability of the various fractions, certainly too uniform to be fortuitous. Since the production of free aldehydic groups is the probable cause of alkali lability, and since the latter reaches a maximum in those fractions where the phosphorus content is lowest, it might be presumed that a portion at least of the phosphate is glycosidically linked in potato amylose. Heterogeneity as regards phosphorus distribution may be tentatively correlated with the length of carbohydrate chains each bearing a glycosidically-linked phosphate. The changes which occur in this series of cells can hardly be attributed to hydrolysis of the amylose-phosphoric acid by hydrogen or hydroxyl ions generated about the electrodes, since the *P*H as determined colorimetrically was substantially the same in the compartment where the combined phosphorus is high as where it is low (*i. e.*, approximately 5.3). Any free phosphate ions are known by test to pass through the membranes and be removed by the water passing through the electrode compartments.

Experimental

The potato starch was a good grade imported sample.

In the experiments described under I, the starch was treated with hot alcoholic hydrogen chloride solution, 0.06 g. per cc., with stirring for ten to twelve minutes and subsequently gelatinized at 65° with the requisite amount of ammonium thiocyanate[3b] and precipitated with alcohol. A 3% paste of this material was made in warm water with stirring and placed in the electrophoretic cell.

In experiments described under II, the membranes were graded commercial variety marketed by Pfaltz and Bauer, New York City. To avoid clogging the more permeable (0.5 to 3.0 μ) membrane was placed on top, separated from the under and less permeable membrane (10 to 50 millimu) by a disk of filter paper. The starch solutions in the special Buchner (Pfaltz and Bauer) funnel above the filtering medium was kept well agitated by a motor-driven stirrer while suction was applied to the filter flask below.

For the mechanical disintegration described under III, a "colloid mill" of the type having disk rotors revolving with little clearance at high speed in opposite directions and surrounded by a water-cooled jacket was used. The machine was made available through the courtesy of Mr. M. P. Hofmann of the U. S. Colloid Mill Corporation of Long Island City, N. Y.

The technique described under IV was exactly that given by Baldwin, whose results were corroborated.

The phosphorus was determined after wet digestion in a Kjeldahl flask according to Neuman[17] in nitric acid to which was added subsequently sulfuric acid and ammonium nitrate. Digestion was carried to the cessation of evolution of brown oxides of nitrogen and the appearance of clear yellow liquid. Fresh additions of acid were often necessary during the digestion.

The digested liquid was made up then to 100 cc. with water, neutralized to methyl red with ammonia, made slightly acid with nitric acid, warmed to 70°, 30 cc. of ammonium molybdate reagent[18] added and the mixtures allowed to stand overnight. The phosphomolybdate precipitate was filtered through a Jena fritted glass funnel and washed free of acid with 1% potassium nitrate solution. The phosphorus was determined alkalimetrically or oxidimetrically. The samples taken usually represented between 2 and 4 mg. of phosphorus. On test runs samples of primary potassium phosphate were analyzed to check the method. The results are given below.

Sample contained 3.02 mg. phosphorus: found 3.24, 3.15 alkalimetrically; and 3.20, 3.14 oxidimetrically.

The alkali labile determinations were made by the method of Taylor and Salzmann.[8]

When the amount of residue unattacked by alkali was desired, it was precipitated by acetone, dried and weighed. For more critical work the amount destroyed was estimated iodimetrically and the results expressed in mg. of iodine consumed per 100 mg. of sample.

Conclusions

1. The absence of any insoluble material in potato starch in the sense in which it is present in cereal starches, is established by several different procedures.
2. Organic phosphorus is shown to be randomly distributed in potato starch, and this circumstance must arise from a diversity of relatively simple and very similar amylose-phosphates.

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(17) Plimmer and Bayliss, *J. Physiol.*, **33**, 439 (1905).

(18) Fales, "Inorganic Quantitative Analysis," The Century Co., New York, 1925, p. 216.

3. Insoluble material is attributable, principally, either to incomplete disorganization of the associated material in the granule or to retrogradation. Both conspire to give the erroneous impression that potato starch contains a non-dispersible fraction comparable to the alpha-amyloses of the cereal starches.

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Alpha Substituted Ethyl *n*-Butyl Ethers[1]

BY HENRY R. HENZE AND JOHN T. MURCHISON

In this Laboratory the alpha chloroalkyl ethers have been studied for the past several years with two major purposes in mind: (1) to extend the series[2] through the synthesis of additional members, as far as seemed practically desirable, securing rather complete physical data relative to the properties of all new compounds; and (2) to investigate the utilization of these alkoxy derivatives in the preparation of new examples of compounds of bifunctional type. In this investigation the preparation, from alpha chloroethyl *n*-butyl ether[2] or alpha cyanoethyl *n*-butyl ether, of representative examples of the more important alkoxy types was effected. The use of the chloro ether in further syntheses was limited because of its rapid hydrolysis and extreme tendency toward complete decomposition upon brief contact with mildly alkaline reagents. However, the cyano derivative is a stable substance which served well as an intermediate for the preparation of other and more important compounds. From the data of the vapor pressures of these new compounds the latent heats of vaporization were calculated. Thermodynamical data have not previously been reported in the literature for compounds of the types of alkoxy ketones, alkoxy esters, etc.

Experimental

Di-*n*-butyl Acetal.—The method of Descudé[3] was adopted, with slight modification, for the synthesis of di-*n*-butyl acetal. Forty-seven grams of alpha chloroethyl *n*-butyl ether was added slowly with shaking and cooling to a solution of twelve grams of sodium in 200 cc. of *n*-butyl alcohol. The mixture was heated on the water-bath at 100° for about fifteen minutes, filtered, washed with distilled water, dried over anhydrous sodium sulfate, and fractionated; b. p. 51° (12 mm.) (corr.); d_4^{20} 0.8296; n_D^{20} 1.4079; M_R calcd., 51.36; M_R found, 51.78.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.89; H, 12.73. Found: C, 69.35; H, 12.71.

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[1] An abstract of the dissertation submitted by John T. Murchison to the Faculty of the University of Texas, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1933.

[2] Henze and Murchison, THIS JOURNAL, **53**, 4077 (1931).

[3] Descudé, *Bull. soc. chim.*, [3] **27**, 1216 (1902).

α-*n*-Butoxyethyl Acetate.—The method of Friedel[4] was employed in this synthesis. A mixture of 49 g. of fused sodium acetate and 48 g. of alpha chloroethyl *n*-butyl ether in 50 cc. of dry benzene was warmed at 60° for fifteen minutes with vigorous shaking. After twelve hours the material was filtered, dried over calcium chloride and distilled under reduced pressure; b. p. 54–54.5° (19 mm.) (corr.); d_4^{20} 0.9122; n_D^{20} 1.4062; MR calcd., 42.32; MR found, 43.14.

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.96; H, 10.07. Found: C, 60.02; H, 9.96.

α-Cyanoethyl *n*-Butyl Ether.—The method used by Gauthier[5] was found satisfactory for this preparation. One hundred and twenty-three grams of cuprous cyanide was suspended in 150 cc. of dry benzene and 150 g. of alpha chloroethyl *n*-butyl ether was added slowly with stirring. The material was warmed at 74–76° for one and one-half hours, cooled, filtered and distilled; b. p. 170–172° (750 mm.) (corr.); d_4^{20} 0.8616; n_D^{20} 1.4040; MR calcd., 35.81; MR found, 36.08.

Anal. Calcd. for $C_7H_{13}ON$: C, 66.08; H, 10.31; N, 11.01; Found: C, 66.02; H, 10.40; N, 11.25.

Preparation of Esters of α-*n*-Butoxypropionic Acid.—A mixture of alpha cyanoethyl *n*-butyl ether, a few drops of water and an excess of the appropriate alcohol was saturated with dry hydrogen chloride, boiled under reflux for ten to fifteen minutes, cooled, filtered, washed with water, and dried over anhydrous potassium carbonate. The dried carbon tetrachloride extract of the wash water was then added and the whole distilled at reduced pressure. The esters were colorless liquids of pleasant odor. The five esters synthesized, together with data concerning them, are listed in Table I.

TABLE I

ESTERS OF α-*n*-BUTOXYPROPIONIC ACID, $CH_3CH(OC_4H_9)COOR$

R	B. p., °C. (corr.)	Mm.	d_4^{20}	n_D^{20}	Molecular refractivity Calcd.	Molecular refractivity Obs.	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found
Methyl	168–169	750	0.9346	1.4090	42.33	42.35	59.97	60.22	10.07	10.00
Ethyl	117–118	52	.9145	1.4100	46.94	47.17	62.02	62.28	10.42	10.46
n-Propyl	204–205	750	.9112	1.4174	51.56	51.97	63.73	63.95	10.70	10.57
n-Butyl	219–221	750	.9058	1.4208	57.18	56.57	65.28	65.18	10.96	10.79
n-Amyl	132–134	38	.9073	1.4268	60.79	61.15	66.60	65.97	11.19	10.95

α-*n*-Butoxypropionamide.—A mixture of 34.5 g. of alpha cyanoethyl *n*-butyl ether, 20 cc. of *n*-propyl alcohol and 40 cc. of dry ether was saturated with dry hydrogen chloride, then warmed on the water-bath, washed with water and dried with anhydrous sodium sulfate. The dried ether extract of the wash water was added and the mixture distilled, b. p. 140–141° (35 mm.); m. p. 24–26°; d_4^{20} 0.9706; n_D^{20} 1.4465; MR calcd., 42.24; MR found, 41.27.

Anal. Calcd. for $C_7H_{15}O_2N$: C, 57.94; H, 10.34; N, 9.65. Found: C, 57.47; H, 10.37; N, 9.80.

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(4) Friedel, *Ber.*, **10**, 492 (1877).

(5) Gauthier, *Compt. rend.*, **138**, 89 (1904).

α-*n*-Butoxypropionic Acid.—A mixture of 34.5 g. of α-*n*-butoxypropionitrile and 100 g. of barium hydroxide in 800 cc. of water was boiled under reflux. After four hours it had become homogeneous; after twenty-three hours it was cooled, acidified with sulfuric acid and filtered. The butoxypropionic acid, which did not separate, was extracted by shaking with two 20 cc. quantities of carbon tetrachloride, dried with calcium chloride and distilled under reduced pressure; b. p. 129–130° (38 mm.); d_4^{20} 0.9842; n_D^{20} 1.4258; M_R calcd., 37.71; M_R found, 38.03.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.50; H, 9.65. Found: C, 57.30; H, 9.47.

The preparation of the butoxypropionic acid from the nitrile by acid hydrolysis was effected but proved less satisfactory than the method recorded above. This acid was also obtained from the α-*n*-butoxypropionamide by saponification with barium hydroxide and subsequent acidification.

Preparation of α-*n*-Butoxy Ketones.—The ketones were obtained from the alpha *n*-butoxypropionitrile by means of the Grignard reaction. The Grignard reagent was prepared in the usual manner, the cyano ether was added gradually with cooling and the mixture was permitted to stand for about sixteen hours. After this material was hydrolyzed by acid the ether layer was separated, washed with sodium bicarbonate solution and dried with anhydrous sodium sulfate. It was possible to distil the methyl, ethyl and *n*-propyl ketones at atmospheric pressure without excessive decomposition but those of higher molecular weight could only be obtained by distillation at reduced pressures.

The ketones synthesized were all liquids of light yellow color, characteristic odor and were miscible with the usual organic solvents. The carbonyl group does not appear to be very reactive for, although the compounds slowly produced a magenta color with Schiff's reagent, not even the methyl ketone could be made to yield a solid bisulfite addition product. All members of this series apparently reacted with phenylhydrazine, *p*-nitrophenylhydrazine and semicarbazide, producing oils which showed no tendency to crystallize. Hence, no further attempt was made to characterize them by preparing other derivatives. The names of the ketones synthesized and the data concerning them are listed in Table II.

TABLE II

n-BUTOXY KETONES, $CH_3CH(OC_4H_9)COR$

R	B. p. °C. (corr.)	Mm.	d_4^{20}	n_D^{20}
Methyl	164–166	750	0.8758	1.4125
Ethyl	80–82	35	.8693	1.4143
n-Propyl	195–197	750	.8685	1.4200
n-Butyl	114–116	35	.8669	1.4247
n-Amyl	129–130	35	.8657	1.4287

R	Molecular refractivity		Analyses, %			
			Carbon		Hydrogen	
	Calcd.	Obs.	Calcd.	Found	Calcd.	Found
Methyl	40.68	40.99	66.51	66.38	11.20	10.96
Ethyl	45.30	45.48	68.29	68.28	11.47	11.51
n-Propyl	49.92	50.16	69.70	69.03	11.71	11.68
n-Butyl	54.54	54.88	70.90	70.76	11.91	11.80
n-Amyl	59.15	59.57	71.93	71.97	12.08	11.91

Vapor Pressures of Alkoxy Compounds.—Although a considerable number of investigators have synthesized examples of various types of alkoxy derivatives, the data concerning the physical properties of these compounds are extremely inadequate, being chiefly limited to a record of boiling point temperatures and, in a few instances, densities and refractive indexes. Since the vapor pressure and latent heat of vaporization are among the more important properties of liquids, these data were secured, as far as was practical, for these derivatives of ethyl *n*-butyl ether.

The vapor pressures, at selected temperatures, of several liquids prepared in the course of this investigation were determined by means of the isoteniscope method suggested by Smith and Menzies.[6] The data so obtained were plotted upon a large scale (curve not shown) using the conventional log $p_{\mathrm{mm.}}$ *vs.* $1/T$ graph, and, selecting the

TABLE III

VAPOR PRESSURE DATA

t, °C.	1/*T*	V. P., mm.	Log V. P.
α-Cyanoethyl *n*-Butyl Ether *A*, 46700; *B*, 8.418			
50	0.003095	7	0.8451
75	.002873	27	1.4314
100	.002680	76	1.8808
125	.002512	197	2.2945
150	.002364	443	2.6464
α-*n*-Butoxypropionic Acid *A*, 52830; *B*, 8.508			
100	0.002680	13	1.1139
125	.002512	38	1.5798
150	.002364	82	1.9138
165	.002282	128	2.1072
200	.002114	474	2.6758
Methyl α-*n*-Butoxypropionate *A*, 51930; *B*, 9.337			
75	0.002873	35	1.5441
100	.002680	95	1.9777
125	.002512	310	2.4914
144	.002398	749	2.8745
Ethyl α-*n*-Butoxypropionate *A*, 53140; *B*, 9.171			
75	0.002873	8	0.9031
100	.002680	54	1.7324
125	.002512	190	2.2788
150	.002364	417	2.6201
165	.002282	682	2.8338
n-Propyl α-*n*-Butoxypropionate *A*, 44190; *B*, 7.647			
100	0.002680	35	1.5441
125	.002512	71	1.8513
150	.002364	154	2.1875
175	.002232	313	2.4955
200	.002114	635	2.8028

t, °C.	1/*T*	V. P., mm.	Log V. P.
n-Butyl α-*n*-Butoxypropionate *A*, 40810; *B*, 6.813			
100	0.002680	12.5	1.0969
125	.002512	28.5	1.4548
n-Amyl α-*n*-Butoxypropionate *A*, 47320; *B*, 7.621			
100	0.002680	10	1.0000
125	.002512	26	1.4150
2-Butoxybutanone-3 *A*, 37860; *B*, 7.819			
50	0.003095	50	1.6990
75	.002873	136	2.1385
100	.002680	315	2.4983
125	.002512	711	2.8519
2-Butoxypentanone-3 *A*, 38760; *B*, 7.833			
60	0.003002	57	1.7559
75	.002873	115	2.0607
100	.002680	263	2.4200
125	.002512	542	2.7340
135	.002450	747	2.8733
2-Butoxyhexanone-3 *A*, 39490; *B*, 7.783			
60	0.003002	39	1.5911
75	.002873	85	1.9294
100	.002680	171	2.2330
125	.002512	378	2.5775
144	.002395	697	2.8432
2-Butoxyheptanone-3 *A*, 10330; *B*, 3.546			
100	0.002680	125	2.0969
125	.002512	154	2.1875
2-Butoxyoctanone-3 *A*, 10330; *B*, 3.130			
100	0.002680	48	1.6812
125	.002512	68	1.8325

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(6) Smith and Menzies, THIS JOURNAL, **32**, 1420 (1910).

best straight line through the points so obtained, the constants A and B in Young's equation, $\log p_{\text{mm.}} = -0.05223\, A/T + B$, were determined by substituting the values of $\log p_{\text{mm.}}$ and $1/T$ selected from the curves. The data from which the latter were plotted and the values obtained for A and B are collected in Table III.

Latent Heats of Vaporization.—The value of the constant A obtained from Young's equation was used in making the calculation, independent of variation in temperature, of the latent heat of vaporization by means of the appropriate form of the Clausius equation $\Delta H = (2.303 \times 1.987 \times 0.05223)A$. The values so obtained are recorded in Table IV.

TABLE IV

LATENT HEATS OF VAPORIZATION

Name	A	ΔH
Alpha cyanoethyl *n*-butyl ether	46700	11160
Alpha *n*-butoxypropionic acid	52830	12630
Methyl alpha *n*-butoxypropionate	51930	12412
Ethyl alpha *n*-butoxypropionate	53140	12700
n-Propyl alpha *n*-butoxypropionate	44190	10562
n-Butyl alpha *n*-butoxypropionate	40810	9754
n-Amyl alpha *n*-butoxypropionate	47320	11310
2-Butoxybutanone-3	37860	9049
2-Butoxypentanone-3	38760	9264
2-Butoxyhexanone-3	39490	9438
2-Butoxyheptanone-3	10330	2469
2-Butoxyoctanone-3	10330	2469

Summary

1. The preparation and properties of the following new compounds are reported: α-cyanoethyl *n*-butyl ether, α-*n*-butoxypropionamide, α-*n*-butoxypropionic acid, the methyl through *n*-amyl esters of this acid, the methyl through *n*-amyl α-*n*-butoxyethyl ketone series, α-*n*-butoxyethyl acetate and the di-*n*-butyl acetal.

2. Vapor pressures were determined at selected temperatures for certain of these compounds and, from these data, the corresponding latent heats of vaporization have been calculated.

AUSTIN, TEXAS

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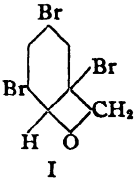
[FROM THE CHEMICAL RESEARCH LABORATORY, HYNSON, WESTCOTT & DUNNING, INC.]

Some Derivatives of Dibromohydroxybenzyl Bromide

BY WILTON C. HARDEN

A comprehensive study of the bromine derivatives of saligenin was made by Auwers and Buttner[1] in 1898, in connection with an investigation of the nature of pseudo phenols. Among the compounds prepared and described by these authors was dibromohydroxybenzyl bromide, dibromosaligenin bromide or dibromosaligenin bromohydrate. This compound, to which Auwers assigned the formula I, is a true pseudo phenol; *i. e.*, its phenolic properties are completely overshadowed by the greater reactivity of bromine in the side chain. Auwers and Buttner prepared many derivatives of this compound, among which were the monomethyl ether, the acetates, the anilide and the piperidine derivatives. In this connection, it should be noted that when the phenolic hydroxyl is replaced by methoxy or acetoxy the reactivity of the side chain halogen is greatly reduced.



I

The purpose of the present paper is to describe some additional derivatives of this compound. In view of the physiological activity and therapeutic usefulness of certain benzyl esters, it was thought that it would be interesting to prepare a series of dibromohydroxybenzyl esters by the reaction between the sodium salts of various acids and dibromosaligenin bromide. Dibromohydroxybenzyl esters of the following acids were hence prepared: benzoic, salicylic, *p*-hydroxybenzoic, *p*-nitrobenzoic, cinnamic, mandelic, succinic and phthalic. These compounds are listed in Table I. A preliminary investigation indicates that several of these esters have valuable physiological properties.

TABLE I

DIBROMOSALIGENIN BROMIDE CONDENSED WITH SODIUM SALTS OF ACIDS

Acids	Dibromohydroxy-	Empirical formula	Mol. wt.	M. p., °C.	Bromine, % Calcd.	Found
Benzoic	Benzyl benzoate	$C_{14}H_{10}O_3Br_2$	386	154	41.45	41.25
Cinnamic	Benzyl cinnamate	$C_{16}H_{12}O_3Br_2$	412	127	38.83	39.12
Mandelic	Benzyl mandelate	$C_{15}H_{12}O_4Br_2$	416	108	38.46	38.27
Succinic	Bis-(benzyl)-succinate	$C_{18}H_{14}O_6Br_4$	646	161	49.53	49.29
Phthalic	Benzyl acid phthalate	$C_{15}H_{10}O_6Br_2$	430	174	37.20	37.06
p-Hydroxybenzoic	Benzyl *p*-hydroxybenzoate	$C_{14}H_{10}O_4Br_2$	402	148	39.80	40.10
p-Nitrobenzoic	Benzyl *p*-nitrobenzoate	$C_{14}H_9O_5Br_2N$	431	153	37.12	36.83
Salicylic	Benzyl salicylate	$C_{14}H_{10}O_4Br_2$	402	156	39.80	40.00

Dibromohydroxybenzyl urea and dibromohydroxyphenylpropionic acid have also been prepared and are shown in Table II.

Since Paterno and Mazzara[2] prepared benzylphenol by the action of

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(1) Auwers and Buttner, *Ann.*, **302**, 131 (1898).

(2) Paterno and Mazzara, *Gazz. chim. ital.*, **3**, 254 (1873).

TABLE II

	Dibromosaligenin bromide condensed with	Product, dibromohydroxy-	Mol. wt.	M. p., °C.
1	Urea	Benzyl-urea	324	207
2	Sodium acetoacetic ester	Phenylpropionic acid	324	117

	Empirical formula	Bromine, % Calcd.	Bromine, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	$C_8H_8O_2Br_2N_2$	49.38	49.50	8.6	8.3
2	$C_9H_8O_3Br_2$	49.38	49.41	...	...

benzyl chloride on phenol in the presence of a small piece of zinc, it seemed worth while to prepare dibromohydroxybenzylphenol by the method of these authors. This compound as well as the corresponding ethers and their acetates and dibromo derivatives are shown in Table III. This reaction is at present being applied to various substituted phenols.

TABLE III

	Product, dibromohydroxy-	Mol. wt.	M. p., °C.	Empirical formula	Bromine, % Calcd.	Bromine, % Found
1	Benzylphenol	358	174	$C_{13}H_{10}O_2Br_2$	44.69	44.83
2	Benzylphenyl ether	358	119	$C_{13}H_{10}O_2Br_2$	44.69	44.90

	Acetate derivatives	M. p., °C.	Acetate Bromine, % Calcd.	Acetate Bromine, % Found	Dibromo derivatives M. p., °C.	Dibromo derivatives Bromine, % Calcd.	Dibromo derivatives Bromine, % Found
1	Diacetate	81	36.20	36.41	198	62.01	61.82
2	Monoacetate	73	40.00	40.10	105	62.01	61.50

Dibromohydroxybenzylphenol readily forms a soluble mono-sodium salt. Although in general the sodium salts of phenols are weak or totally ineffective germicides, a 1% solution of this compound was found to kill *Staphylococcus aureus* in a dilution of 1 to 9.

Experimental

All of the esters shown in Table I were prepared in a similar manner. The preparation of the benzoate will, therefore, serve as a typical example.

One-twentieth mole (7.2 g.) of sodium benzoate was suspended in 50 cc. of dry benzene in a 500-cc. round-bottomed three-necked flask, fitted with stirrer, reflux condenser and dropping funnel; 17.2 g. ($^1/_{20}$ mole) dibromosaligenin bromide, dissolved in 250 cc. of warm benzene, was added drop by drop while the solution was stirred and heated to boiling on the water-bath. After three hours boiling, the sodium bromide was filtered from the hot solution and the filtrate cooled. The ester crystallized at once and was recrystallized from benzene.

Preparation of Dibromohydroxyphenylpropionic Acid.—12.8 g. of acetoacetic ester was dissolved in 100 cc. of dry toluene, stirred mechanically, and 2.3 g. of sodium, cut in small pieces, was added. After formation of the sodium salt of the acetoacetic ester, the solution was cooled to room temperature and 34.4 g. of dibromosaligenin bromide in 100 cc. of dry toluene was added drop by drop. After completion of the reaction, the sodium bromide was removed by filtration and the filtrate concentrated *in vacuo* to remove the solvent. The resulting product was a clear yellow oil of characteristic odor. This was dissolved in alcohol and added to a hot 20% alcoholic solution of potassium hydroxide and finally boiled for three hours. The solution was then cooled, poured into water and made acid. A heavy tar separated, and on standing overnight in the ice-box hardened to a semi-crystalline mass. This was repeatedly recrystallized from water.

Preparation of Dibromohydroxybenzylphenol.—17.2 g. of dibromosaligenin bromide was dissolved in 250 cc. of hot toluene in a 500-cc. round-bottomed, three-necked flask, fitted with mechanical stirrer, reflux condenser, and dropping funnel. A small piece of mossy zinc, previously cleaned by hydrochloric acid, was added, followed by 7.0 g. of phenol in 50 cc. of toluene. The mixture was then heated to boiling until the evolution of hydrogen bromide had practically ceased (about three hours). The toluene solution was then washed with water to remove hydrogen bromide, dried with anhydrous sodium sulfate and concentrated *in vacuo*. The solution was then diluted with one-half its volume of ligroin and cooled in the ice-box. The crystals thus obtained were recrystallized from toluene.

Preparation of Dibromohydroxybenzyldibromophenol.—5.0 g. of dibromohydroxybenzylphenol, prepared as described above, was dissolved in 50 cc. of warm glacial acetic acid and 5 g. of bromine added drop by drop. The solution was allowed to stand at room temperature for several hours and finally cooled in ice. The resulting white crystals were recrystallized from acetic acid.

Preparation of Dibromohydroxybenzyl Phenyl Ether.—The filtrate from the preparation of dibromohydroxybenzylphenol was steam distilled to remove the toluene and ligroin. The resulting heavy oil was crystallized repeatedly from dilute alcohol. After refluxing for three hours with acetic anhydride in the presence of anhydrous sodium acetate, this compound yielded only a mono-acetate, indicating the formula assigned it.

The author wishes to acknowledge the valuable assistance of Mr. Grant Spurrier, who performed many of the analyses.

Summary

1. A number of derivatives of dibromosaligenin bromide have been prepared.

2. A preliminary investigation indicates that certain of these derivatives possess valuable pharmacological properties.

BALTIMORE, MARYLAND

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[CONTRIBUTION NO. 91 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Occurrence of a New Case of Isomerism in the Fluorenone Carboxylic Acid Series: Isomeric Products from the Action of Sulfuric Acid upon 3,3′-Dichlorodiphenic Acid

BY ERNEST H. HUNTRESS, IVAN S. CLIFF AND EDWARD R. ATKINSON

The Effect of Acetic Anhydride and of Concentrated Sulfuric Acid upon 3,3′-Dichlorodiphenic Acid.—In the course of some work upon 3,3′-dichlorodiphenic acid[1] we had occasion to examine its behavior with acetic anhydride and with concentrated sulfuric acid. With the former it readily yielded a monomolecular anhydride which has been reported in the earlier paper. Upon turning to the action of sulfuric acid, however, we found that two distinct but isomeric products were formed according to the temperature employed. One of these substances (formed at 125°) appears to be

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(1) Huntress and Cliff, THIS JOURNAL, 55, 2559–2567 (1933).

the expected keto acid for it titrates readily, easily forms the corresponding acid chloride and amide, and on heating loses carbon dioxide to give a dichlorofluorenone. The details of this behavior have also been described in the cited reference.

The product obtained at a higher temperature (170°), however, appears also to be a dichlorofluorenone carboxylic acid. Its analysis for chlorine is identical with that of the expected keto acid, its molecular weight is the same as that of the isomeric keto acid, and it definitely contains a carboxyl group as shown by the formation of an acid chloride and an amide. Moreover, it certainly contains a ketone group for not only is it colored yellow like other fluorenone carboxylic acids but it readily yields an oxime. We have, therefore, two isomeric monobasic acids prepared at different temperatures by the same procedure from the same starting material when the conventional theory will account for only one. For reasons which will appear we choose to regard as the true keto acid that dichlorofluorenone carboxylic acid obtained at the lower temperature; the isomer produced at the higher temperature we have temporarily designated as "Acid X."

It is a surprising fact that these two isomeric acids melt without evidence of decomposition at exactly the same temperature (242.5° uncorr.); nevertheless the melting range of approximately equal parts of the two individuals is broad and far depressed, *viz.*, 205–208°, 195–200°, 200–205° in various experiments. The conviction that these two acids are really different individuals is furthermore supported by their conversion to analytically isomeric acid chlorides which melt at slightly different temperatures and depress each others melting points, and the conversion of these acid chlorides to the corresponding amides which in turn give identical analyses and have different melting points but whose mixture fuses far below that of either individual. These facts are included in the following Table I.

TABLE I

MELTING POINTS AND MIXED MELTING POINTS

	Parent substance	Acid			Acid chloride		Acid amide
A	Keto acid (from 3,3′-dichlorodiphenic acid)	242.5			180–181		280–281
B	Mixtures of A and C	205–208	195–200	200–205	140–145		255–260
C	"Keto acid X"	242.5			183–184		296
D	Mixtures of C and E	235–239			178–180		292–294
E	"Hunn's keto acid" (from 5-5′-dichlorodiphenic acid)	240			185		301
F	Mixtures of A and E	205–208			145–150	150–155	250–252

During the early part of the work the two isomeric acids had been recrystallized from different solvents and it was thought possible that they were different crystalline forms. Interchange of solvents, however, effected no change in original melting point nor upon the melting point of the mixture. Furthermore, when the keto acid formed at 125° was redissolved in sulfuric acid and heated under the same conditions which were known to yield "Acid X" directly from the original 3,3'-dichlorodiphenic acid, there was isolated a good yield (67%) of resultant product which was identical with "Acid X" as evidenced by its depression of the melting point of the keto acid and its failure to depress the melting point of a sample of "Acid X" prepared in the usual manner. It thus is evident that the keto acid can be converted into "Acid X."

We are inclined to regard as the "true" keto acid that produced at the lower temperature on three principal grounds. First it titrates very smoothly in neutral alcohol yielding neutralization equivalents which closely check the theoretical, whereas "Acid X," although soluble in alkalies and even in sodium bicarbonate solution, behaves very strangely when titrated in alcohol, giving poor end-points and erratically variant numerical results. Second, on heating above its melting point the keto acid obtained at the lower temperature smoothly evolves carbon dioxide and yields as principal product 1,6-dichlorofluorenone, whereas "Acid X" under precisely the same conditions sublimes almost unchanged. Third, since the so-called "Acid X" appears to be preparable from the so-called keto acid it seems probable that any abnormal rearrangement would be produced at the higher temperature rather than at the lower.

In speculating as to the probable reason for the appearance of two isomeric series of derivatives, the first thought is that the "Acid X" might be the corresponding anhydride of the 3,3'-dichlorodiphenic acid produced by the dehydrating action of the sulfuric acid. That this cannot be the explanation, however, is evidenced by the previous preparation of this product in normal fashion. It was colorless, melted at 257–258° uncorr., gave correct analysis for chlorine, did not dissolve in sodium carbonate solution, did dissolve in an alkali, and these solutions on acidification reprecipitated 3,3'-dichlorodiphenic acid. Furthermore the melting point of a mixture of "Acid X" with this authentic anhydride was markedly depressed. A second suggestion that "Acid X" might be the bimolecular anhydride of the keto acid formed from 3,3'-dichlorodiphenic acid at 125° is also inadmissible, for a determination of its molecular weight in camphor yielded a result consistent only with the presence of one fluorenone nucleus. A third hypothesis would ascribe the supposed isomer to the presence in the original raw material of another isomeric dichlorodiphenic acid. Against this view we can urge the following considerations. 1. The 3,3'-dichlorodiphenic acid was carefully purified. Moreover it had been prepared by a series of synthetic steps in which each intermediate had been carefully purified. The original commercial intermediate from which the series had started was a homogeneous material. 2. The yields of "Acid X" readily obtainable were such as to preclude the possibility of its origin from an impurity. For example, 31% of pure product was obtained after reprecipitation from sodium bicarbonate solution and recrystallization from glacial acetic acid.

Since carbon dioxide could not be eliminated from "Acid X" either by heating alone or with soda lime, the carboxyl group was finally replaced by hydrogen by means of conversion of the amide to the amine, diazotization and boiling with alcohol. This series of operations yielded 1,6-dichlorofluorenone identified by analysis, by melting point, by mixed melting point with an authentic sample, by conversion to the oxime and mixed melting point of the latter with an authentic specimen. This result shows that during the isomerization to "Acid X" both the fluorenone nucleus and the relative position of the two halogen atoms in it are preserved.

The Effect of Acetic Anhydride and of Concentrated Sulfuric Acid upon 5,5′-Dichlorodiphenic Acid.—When 5,5′-dichlorodiphenic acid is refluxed with acetic anhydride the corresponding diphenic anhydride readily forms in good yield.[2] In an earlier paper we have shown[3] that at 400° this anhydride evolves carbon dioxide and yields 3,6-dichlorofluorenone.

Upon heating 5,5′-dichlorodiphenic acid with concentrated sulfuric acid at 125°, *i. e.*, under the same conditions which transformed 3,3′-dichlorodiphenic acid to the keto acid condensation product, we have obtained here also a keto acid which, although not reported by him, may conveniently be designated as "Hunn's keto acid." Although this substance yielded a corresponding acid chloride and amide and the melting points both of the acid and of its derivatives are of the same general magnitude as those noted for the products from the 3,3′ series, yet the melting points of mixtures of corresponding compounds of the "Acid X" series and the Hunn's keto acid series were slightly though definitely depressed. This observation appears to eliminate the possibility that the formation of "Acid X" might be due to the presence of 5,5′-dichlorodiphenic acid or its reaction products in the original material. Furthermore, the melting points of mixtures of compounds of the keto acid series with the corresponding compounds of the Hunn's keto acid series were greatly depressed. These observations are all included in Table I.

The Examination of Other Dichlorodiphenic Acids for Possible Isomeric Keto Acids.—Having observed this formation of isomeric materials in the sulfuric acid treatment of 3,3′-dichlorodiphenic acid, we have also examined in a preliminary way the possibility that an analogous situation would appear with other dichlorodiphenic acids. Of the three other possible symmetrically substituted dichlorodiphenic acids, we already had available a sample of the 5,5′-dichloro isomer from another part of the work. A sample of 6,6′-dichlorodiphenic acid prepared according to the method of Christie, James and Kenner[4] was made available to us through the courtesy of Prof. A. A. Morton. 4,4'-Dichlorodiphenic acid, not previously reported in the literature, was synthesized from 5-chloro-2-aminobenzoic acid by the same method used for the 3,3'-isomer.

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[2] Hunn, THIS JOURNAL, **45**, 1024–1030 (1923).

[3] Ref. 1, p. 2566.

[4] Christie, James and Kenner, *J. Chem. Soc.*, **123**, 1948 (1923).

With the 4,4'- and the 5,5'- isomers the reaction product obtained by the action of concentrated sulfuric acid at 125° appeared to be the same as the product obtained at 175° in the respective cases. The corresponding keto acid was formed in each instance but the melting point of mixtures of the products from different temperatures was not depressed. It will be noted that in the case of 6,6'-dichlorodiphenic acid there would presumably be no possibility of fluorenone carboxylic acid formation by a ring closure process, for the necessary positions are filled with chlorine atoms. As a matter of fact we found that this 6,6'-dichlorodiphenic acid when heated with concentrated sulfuric acid at 175° for thirty minutes gave only a slight coloration in the resultant solution, evolved no gas, and was recovered unchanged upon dilution.

Experimental Part

All melting points reported in this paper were taken by the method described in Mulliken's "Identification of Pure Organic Compounds," Vol. I, page 218, on a 360° rod form melting point thermometer immersed in the sulfuric acid to the 0° point.

3,3'-Dichlorodiphenic Acid.—This acid was prepared exactly as described in an earlier paper.[5]

The New Keto Acid from 3,3'-Dichlorodiphenic Acid. ("Acid X.")—Two grams of 3,3'-dichlorodiphenic acid (m. p. 299–300°) was added to 5 ml. of pure concentrated sulfuric acid in a small flask and heated in an oil-bath at 170 ± 1° for one hour. The deep reddish-brown solution was observed to give off bubbles of gas during the heating. Finally, the sulfuric acid solution was poured onto cracked ice and the grayish-yellow precipitate filtered off, washed with water until free from sulfate and dried at 110°. The crude product melted at 195–200° and weighed 1.88 g. corresponding to a quantitative yield of keto acid. For purification it was dissolved in 100 ml. of 1 *N* sodium bicarbonate solution at 50°, filtered, and reprecipitated by acid. Only a trace of insoluble material remained and 1.8 g. of acid was reprecipitated from the alkaline solution. Recrystallization from hot glacial acetic acid after brief treatment with Norite decolorizing carbon yielded 1.0 g. of yellowish-gray product, m. p. 241°. Repeated recrystallization from hot glacial acetic acid will raise the melting point to 242.5° uncorr.

The results of analysis and molecular weight were as follows: *Anal.* Calcd. for $C_{14}H_6Cl_2O_3$: Cl, 24.23. Found: 24.47, 24.30; on a different sample, 24.32, 24.16. Calcd.: C, 57.34; H, 2.05. Found: C, 57.45, 57.41; H, 2.55, 2.51. *Mol. wt.* (Rast method in camphor) Calcd., 293. Found: 300, 290, 290.

All attempts to get consistent results on titration of "Acid X" have so far been unsuccessful. Titrated directly in aqueous suspension with *N*/10 sodium hydroxide using phenolphthalein gave values of 316.1 and 314.5. The same sample dried at 110° for two hours and titrated in neutral alcohol gave 299.8 and 301.4. After recrystallizing the sample twice from glacial acetic acid and repeating the titration in alcohol, the values obtained were 283.6 and 281.1. After still another recrystallization from glacial acetic acid the neutralization equivalents in alcohol were 266.4, 274.7 and 266.6. None of these values come very near the theoretical of 293. The titration liquors from these

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(5) Ref. 1, p. 2561.

last three runs were combined, acidified, and the precipitated acid recrystallized from glacial acetic acid: the product melted 242.5–243.0° as in the first place. A different sample of "Acid X" similarly titrated in alcohol gave values of 285.8 and 285.6. If dissolved in excess standard sodium hydroxide by heating at 90° for one minute and measured by titrating the excess alkali, this sample gave values of 275.2 and 281.1. In all the above titrations phenolphthalein was employed. The end-point was very indefinite and difficult to fix with certainty, contrasting sharply with the normal precise end-point noted with the isomeric keto acid of our earlier paper.[6]

It will be recalled that the melting point of the keto acid obtained from 3,3′-dichlorodiphenic acid by the action of sulfuric acid *at 125°* was observed to be 242.5° and that the corresponding constant for the "Acid X" obtained in a similar manner *at 170°* is precisely the same, *viz.*, 242.5°. Nevertheless, mixtures of equal weights of the two isomeric substances were strongly depressed and the effect was confirmed in three separate experiments, the melting range of the mixture being observed at 205–208°, 195–200° and 200–205°, respectively.

Since the keto acid had been recrystallized from alcohol, while the "Acid X" had been purified from glacial acetic acid, an experiment was made to determine whether interchange of solvents would have any effect. For this purpose a sample of pure keto acid (previously prepared from alcohol) was recrystallized from hot glacial acetic acid; and a sample of pure "Acid X" (previously prepared from acetic acid) was recrystallized from hot alcohol with addition of water. After this procedure each recovered product possessed its original melting point and did not depress the melting point of its corresponding original. Mixtures of the recrystallized keto acid and "Acid X," however, showed the same marked depression of melting point observed in the original samples.

Conversion of Keto Acid to "Acid X."—A sample of 1.65 g. of absolutely pure keto acid, m. p. 242.0–242.5°, prepared at 125° was redissolved in 4.0 ml. of pure concentrated sulfuric acid and heated for one hour at 170 ± 1° (*i. e.*, under the conditions which had yielded "Acid X"). The yield of crude was 1.4 g., m. p. 212–215° dec.; after dissolving in sodium bicarbonate solution without appreciable residue acidification threw down 1.2 g. of dull yellow solid, m. p. 220–225° dec. After recrystallization from glacial acetic acid there was obtained 1.1 g. of light yellow acid, m. p. 241–242°. This sample failed to depress the melting point when mixed with authentic "Acid X," but depressed that of an authentic sample of keto acid to 203–205°.

The Acid Chloride of "Acid X."—One and three-tenths grams of pure "Acid X," m. p. 242.5°, was refluxed for two hours with 5.3 g. of pure thionyl chloride. On cooling the clear solution deposited bright yellow crystals, m. p. 183–184° uncorr. This melting point was unchanged upon further recrystallization from anhydrous benzene.

Anal. Calcd. for $C_{14}H_5Cl_3O_2$: Cl, 34.19. Found: 34.31, 34.10.

The melting point of a mixture of approximately equal parts of the keto acid chloride (m. p. 180–181°) with the "Acid X" chloride (m. p. 183–184°) was depressed to 140–145°.

The Amide of "Acid X."—A small sample (0.4 g.) of pure acid chloride from "Acid X" was shaken with excess concentrated ammonium hydroxide in the cold, and the insoluble residual solid filtered and washed with water. Recrystallization from hot alcohol by partial precipitation with water gave the amide (0.3 g.) as a cream colored solid, m. p. 296° uncorr.

Anal. Calcd. for $C_{14}H_7Cl_2NO_2$: Cl, 24.29. Found: 24.45, 24.62.

The melting point of a mixture of equal parts of the keto acid amide (m. p. 280–281°) with the "Acid X" amide (m. p. 296°) was depressed to 255–260°.

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(6) Ref. 1, p. 2564.

The Oxime of "Acid X."—Three-tenths of a gram (0.001 mole) of "Acid X" (m. p. 242.5°) was dissolved in 5 ml. of 1 *N* sodium bicarbonate and a solution of 0.43 g. (0.010 mole) of hydroxylamine hydrochloride in 5 ml. of alcohol was added. After refluxing for fifteen minutes 50 ml. of water was added to the clear solution, precipitating 0.28 g. (85% theoretical) of cream colored oxime. After dissolving in 10 ml. of acetone and reprecipitating with 10 ml. of hot water the melting point remained constant at 286° dec. uncorr.

Anal. Calcd. for $C_{14}H_7Cl_2NO_3$: Cl, 23.02. Found: 22.92, 22.92.

The substance is difficultly soluble in cold ether or hot water, slightly soluble in alcohol, very soluble in acetone.

The Amine from "X Acid" Amide.—One and six-tenths grams (0.0055 mole) of "X acid" amide was made into a smooth paste with 20 ml. of water. This paste was then added to a solution of sodium hypobromite prepared from 1.3 g. (0.0081 mole) of bromine, 3.0 g. (0.075 mole) of sodium hydroxide, and 20 ml. of water and the ice cold mixture allowed to stand for two hours. After filtering off a small amount of undissolved solid, the red-brown filtrate was heated at 100° for two hours causing the precipitation of a brick-red crude weighing 0.82 g. (57% theoretical) and melting 245–255° uncorr. This melting point was unchanged by recrystallization from alcohol, but after boiling with alcoholic sodium hydroxide for twenty minutes a homogeneous red solid, m. p. 229–230° uncorr., was obtained.

Anal. Calcd. for $C_{13}H_7Cl_2NO$: Cl, 26.90. Found: 27.36, 26.95.

The melting point of a mixture of this amine with that from 1,6-dichlorofluorenone-5-carboxylic acid amide (keto acid amide) was depressed to about 190°.

1,6-Dichlorofluorenone from the Amine Corresponding to "Acid X."—Three-tenths gram (0.0114 mole) of the above amine was suspended in 30 ml. of alcohol and treated with 3 ml. of concentrated hydrochloric acid plus 2 ml. of water. Much of the amine dissolved in the alcohol to give a solution which turned grayish-yellow on addition of acid. To the ice cold mixture was slowly added a concentrated solution of 0.1 g. of sodium nitrite until a definite excess was noted. After standing for thirty minutes, 0.1 g. of copper bronze was added and the mixture allowed to stand overnight. The next morning 0.24 g. (85% theoretical) of crude 1,6-dichlorofluorenone melting at 205–206° was filtered off. After one recrystallization from benzene and subsequent vacuum sublimation, 0.15 g. of pure ketone melting at 217.5° uncorr. was obtained.

Anal. Calcd. for $C_{13}H_6Cl_2O$: Cl, 28.48. Found: Cl, 28.46, 28.28.

A mixture of the above product with authentic 1,6-dichlorofluorenone also melted at 217.5° uncorr. As final proof of the identity of the compound it was converted to the oxime in the usual manner. This melted at 230° uncorr. dec. and failed to depress the melting point of an authentic sample.

1,6-Dichloro-5-aminofluorenone.—This is the amine corresponding to the so-called "keto acid amide." It was prepared by substantially the same process used for the corresponding "X acid" derivative above; yield, 62%; m. p. 257° uncorr. It crystallized from alcohol in salmon-colored crystals of entirely different appearance from the isomeric derivative.

Anal. Calcd. for $C_{13}H_7Cl_2NO$: Cl, 26.90. Found: 27.02, 26.72.

5,5'-Dichlorodiphenic Acid. (Hunn's Acid) (I).[7]—This acid, previously reported by Hunn according to an entirely different procedure, was prepared by us in a manner analogous to that employed for 3,3'-dichlorodiphenic acid. This process started with commercial 4-chloro-2-aminotoluene hydrochloride ("Fast Red KB Base" of the General Dyestuffs Corporation) and passed through 4-chloro-2-acetylaminotoluene, 4-chloro-2-

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(7) Hunn, THIS JOURNAL, 45, 1024–1033 (1923).

acetylaminobenzoic acid, and 4-chloroanthranilic acid to the desired diphenic derivative. The original base hydrochloride with acetic anhydride in glacial acetic acid solution gave 78% yield of acetyl derivative, m. p. 130° (as recorded). Oxidation of the latter according to the procedure indicated for the 6-chloro isomer[8] gave an 85% yield of 4-chloro-2-acetylaminobenzoic acid, m. p. 213° (recorded 214°). This was hydrolyzed by boiling two hours with 9 *N* hydrochloric acid and the nearly quantitative yield of 4-chloroanthranilic acid hydrochloride diazotized and coupled according to the method used by Hunn for a different intermediate. The melting point of the 5,5′-dichlorodiphenic acid so obtained could not be raised above 291° uncorr. although Hunn reports 297° for his product.

1,6-Dichlorofluorenone-4-carboxylic Acid (II).—The keto acid from Hunn's acid. Although Hunn reported the preparation of the anhydride corresponding to 5,5′-dichlorodiphenic acid he neglected to deal with the corresponding keto acid, which we have therefore prepared. Five grams (0.016 mole) of pure 5,5′-dichlorodiphenic acid was mixed with 12 ml. of pure concentrated sulfuric acid and the solution heated at 125 ± 1° for one hour. The dark brownish-red solution was then poured onto ice, and the precipitated acid filtered, washed free from sulfate and dried. The crude acid weighed 4.7 g. (100% theoretical) and melted 228–230°. The product was dissolved in 100 ml. warm 1 *N* sodium bicarbonate solution, filtered and reprecipitated with 6 *N* sulfuric acid. The product which first separated proved to be the difficultly soluble sodium salt of the keto acid, which after filtration was converted to the free acid by digestion with 6 *N* sulfuric acid. There was thus obtained 4.4 g. of pale yellow acid, m. p. 235–236°. After recrystallization from 40 ml. of boiling alcohol with addition of 5 ml. of water, 3.2 g. of pure keto acid, m. p. 240°, was obtained and this melting point was not raised by further recrystallization.

Anal. Calcd. for $C_{14}H_6Cl_2O_3$: Cl, 24.23. Found: 24.21, 24.23. Neut. equiv. (in alcohol) Calcd., 293.0. Found: 293.6, 293.7.

A mixture of this keto acid (m. p. 240°) with an equal amount of 1,6-dichlorofluorenone 5-carboxylic acid (m. p. 242.5°)[6] showed a melting point depressed to 205–208°. A mixture of this keto acid (m. p. 240°) with the "Acid X" was (slightly) depressed to 235–239° and this observation was checked in a second experiment.

1,6-Dichlorofluorenone-4-carboxylic Acid Chloride.—Early attempts to prepare this acid chloride by the method employed with the keto acid from 3,3′-dichlorodiphenic acid led only to products which gave unsatisfactory analyses for chlorine. It was noted that when this keto acid was treated with thionyl chloride the immediate reaction was far more vigorous than in the two other isomeric cases. Satisfactory results were finally obtained by dissolving 1 g. (0.0034 mole) of pure 1,6-dichlorofluorenone-4-carboxylic acid in 3.7 g. (0.034 mole) of thionyl chloride and refluxing for one hour (instead of two as in the other cases). On cooling the solution 0.65 g. of clear yellow solid precipitated corresponding to 61% yield. After reprecipitation from boiling benzene with petroleum ether the melting point remained constant at 185° uncorr.

Anal. Calcd. for $C_{14}H_5Cl_3O_2$: Cl, 34.19. Found: 34.41, 34.31.

A mixture of this keto acid chloride with the corresponding derivative from "Acid X" melted at 178–180° uncorr.

1,6-Dichlorofluorenone-4-carboxylic Acid Amide.—A small sample of crude acid chloride was converted to amide by boiling with concentrated ammonium hydroxide, cooling and filtering off the insoluble solid, m. p. 268–270°. After three recrystallizations from dilute alcohol the melting point reached a constant maximum of 301° uncorr.

Anal. Calcd. for $C_{14}H_7Cl_2NO_2$: Cl, 24.29. Found: 24.39, 24.72.

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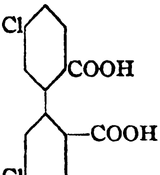
[8] Ref. 1, p. 2562.

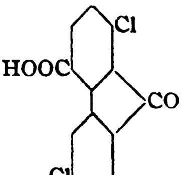
The melting point of a mixture of equal parts of this amide (m. p. 301°) with the "X acid" amide (m. p. 296°) was depressed to 292–294°.

Attempts to Obtain 1,6-Dichlorofluorenone from 1,6-Dichlorofluorenone-4-carboxylic Acid.—It will be recalled that when 1,6-dichlorofluorenone-5-carboxylic acid (that from 3,3′-dichlorodiphenic acid) was heated to 350° for one hour it readily lost carbon dioxide and yielded 1,6-dichlorofluorenone. When exactly the same conditions and procedure[9] were applied to 1,6-dichlorofluorenone-4-carboxylic acid (Hunn's keto acid), however, very little carbon dioxide was evolved and after sublimation in vacuum the sublimate was found to be soluble in dilute sodium carbonate solution and to consist of unchanged keto acid. Upon raising the temperature to 400° and heating for half an hour under atmospheric pressure much charring occurred and a pure homogeneous product could not be obtained. The difference in the ease of loss of carbon dioxide from these two keto acids is notable.

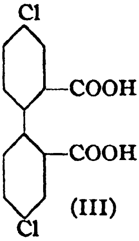
4,4′-Dichlorodiphenic Acid.—This previously unreported dichlorodiphenic acid (III) was synthesized from 5-chloro-2-aminobenzoic acid (5-chloroanthranilic acid) by the same method used for the 3,3′-isomer. The necessary substituted anthranilic acid was obtained from the interaction of sulfuryl chloride and anthranilic acid according to the directions of Eller and Klemm.[10] Yields of 4,4′-dichlorodiphenic acid were about 50%. The pure product crystallizes from 50% alcohol in white needles, m. p. 264–265° uncorr. It is insoluble in water, but soluble in alcohol, ether or glacial acetic acid.



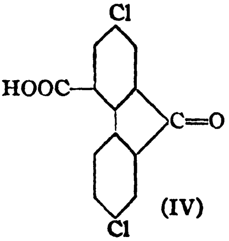
(I)



(II)



(III)



(IV)

Anal. Calcd. for $C_{14}H_8Cl_2O_4$: Cl, 22.83. Found: 22.88, 23.24. Neut. equiv. Calcd., 155.5. Found: 155.2, 156.4.

As impurities from the coupling of the diazotized chloroanthranilic acid there were isolated 2,5-dichlorobenzoic acid, 2-hydroxy-5-chlorobenzoic acid and an unidentified substance of m. p. 320°.

4,4′-Dichlorodiphenic Anhydride.—The corresponding dichlorodiphenic acid was refluxed thirty minutes with excess acetic anhydride. The acid soon dissolved and on cooling the desired anhydride separated out in colorless crystals. After recrystallization from a mixture of acetic anhydride and glacial acetic acid, it was washed with dry ether and dried at 100°; m. p. 308–310° uncorr.

Anal. Calcd. for $C_{14}H_6Cl_2O_3$: Cl, 24.23. Found: 24.20, 24.36.

Upon heating above 330° for fifteen minutes, the anhydride sublimed readily with some loss of carbon dioxide and appearance of a yellow product presumably consisting of a dichlorofluorenone. This substance was not further investigated in this research.

2,7-Dichlorofluorenone-4-carboxylic Acid.—This substance (IV) has previously been reported under the designation x,x-dichlorofluorenone-4-carboxylic acid.[11] It was readily prepared by heating one gram of the 4,4′-dichlorodiphenic acid with 15 ml. of concentrated sulfuric acid at 150–170° for thirty minutes. The resulting deep reddish-

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(9) Ref. 1, p. 2565.

(10) Eller and Klemm, *Ber.*, 55, 217–224 (1922).

(11) Beilstein, 4th edition, 1st Suppl., Vol. X, p. 370.

brown solution was cooled, poured onto ice and the precipitated acid filtered off and washed. After recrystallizing from 50% alcohol it was obtained as a yellow solid, m. p. 248–249° uncorr.

Anal. Calcd. for $C_{14}H_6Cl_2O_3$: Cl, 24.23. Found: 24.18, 24.42. Neut. equiv. Calcd., 293. Found: 294, 294.

In order to examine the possible formation of isomers during this conversion, a test was made in which 0.1 g. of 4,4′-dichlorodiphenic acid was heated with 75 drops of concentrated sulfuric acid at 125° for forty-five minutes, another sample at 175° for thirty minutes and a third at 225° for fifteen minutes. The products from the first two runs were identical, melted at 248° uncorr., and failed to depress this value when mixed. At 225° or above, however, escape of carbon dioxide was noted and the crude product consisted of a mixture of the expected keto acid with 2,7-dichlorofluorenone. The former was easily separated by virtue of its solubility in sodium bicarbonate solution; the insoluble ketone which remained was recrystallized from 50% alcohol and identified by means of its melting point and color.[12] At 265–270° all of the keto acid was decomposed, the solid product obtained consisting exclusively of ketone accompanied by a small amount of its water-soluble sulfonation product.

Summary

1. When 3,3′-dichlorodiphenic acid is heated with concentrated sulfuric acid at 170° there is formed a keto carboxylic acid isomeric with, but different from, the 1,6-dichlorofluorenone-5-carboxylic acid which is quantitatively obtained at 125°.

2. This latter keto acid can be converted to the new isomeric keto acid by heating in concentrated sulfuric acid at the higher temperature.

3. Not only are these two acids definitely different but they yield different though isomeric acid chlorides and amides, and the latter degrade by the Hofmann reaction to isomeric but different amines.

4. The amino compound thus obtained from "Acid X" deaminates to yield 1,6-dichlorofluorenone, indicating that during the formation of "Acid X" both the fluorenone nucleus and the relative positions of the two halogen substituents therein are unchanged.

5. Since preliminary experiments have failed to detect the existence of a corresponding situation with the 4,4′-, 5,5′-, or 6,6′-dichlorodiphenic acids it may be that the phenomenon is associated with the 3,3′-position of the substituent groups.

6. In the course of this work the following new compounds have been reported: the new keto acid from 3,3′-dichlorodiphenic acid, its acid chloride, its amide, the corresponding amine, the "X Acid" oxime: 1,6-dichlorofluorenone-4-carboxylic acid, its acid chloride and amide; 1,6-dichloro-5-aminofluorenone; 4,4′-dichlorodiphenic acid, 4,4′-dichlorodiphenic anhydride and 2,7-dichlorofluorenone-4-carboxylic acid.

CAMBRIDGE, MASSACHUSETTS

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[12] *Cf.* Schmidt and Wagner, *Ann.*, **387**, 161 (1911); Courtot, *Ann. chim.*, [10] **14**, 96 (1930).

[A CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Quantitative Hydrogenation at 100–300 Atmospheres

BY HOMER ADKINS

Suitable apparatus apparently has not yet been described for the quantitative measurement of the absorption of hydrogen by an organic compound over a catalyst at pressures above a few atmospheres. Such an apparatus would be useful for several purposes, *viz.*, the determination of the degree of unsaturation of a substance such as carotene; the determination of the amount of an unsaturated compound in a mixture, as for example in the estimation of the amount of a pyridine in the presence of a piperidine derivative; in the selection of optimum conditions for and the control of the hydrogenation of compounds available in quantities of only a few thousandths of a mole. An apparatus satisfactory for these purposes must have a small internal volume and be absolutely hydrogen tight at pressures up to 200 atmospheres and temperatures up to 250°. In addition it should be safe and simple, and as inexpensive as possible. Such a piece of equipment has been in use in this Laboratory for some time and its construction and use are described below.

The design of the bomb and assembly has been modified from that previously described[1] for the sake of economy of construction, and convenience in use, as well as to meet the necessity for a small internal volume in quantitative work. These changes involve first, the elimination of the liner and the use of a small bent copper tube to prevent the catalyst and liquid from entering the hydrogen line and gage; second, the location of the thermocouple well in the wall of the bomb instead of as a separate unit which entered the bomb cavity. These two changes have reduced the cost of a small outfit to less than one-half of that of the former type. The location of the thermocouple in the wall of the bomb also results in a more even temperature control of the contents of the bomb. Much more important, however, is the fact that the copper gasket is now so much smaller in diameter that it is more readily crushed and the possibility of leakage practically eliminated. These advantages have been utilized not only in a bomb for quantitative work, but also in one for hydrogenations involving up to 80 ml. of material, a capacity which is very useful in preparational work. This type of bomb may be used either with a spiral of steel tubing for the introduction of hydrogen while the bomb is in motion, or with the simpler and more inexpensive gage assembly described below.

The dimensions of the two bombs are given in Table I, a cross section of one in Fig. 1 and a photograph of the assembled apparatus in Fig. 2. The gage assembly consists of the following parts: a hydraulic gage 3.5 inches in diameter calibrated to 5000 lb. per sq. in. (or 10,000 for pressures of 200–300 atmospheres) as supplied by the United States Gage Company, 44 Beaver Street, New York, is screwed against a copper gasket in a three-way superpressure needle valve supplied by the American Instrument Company, 774 Girard Street, Washington, D. C. The openings in this valve are so placed that when the valve is closed no gas pressure is exerted on the valve packing. A 7-cm. nipple of 6.3 × 1.6 mm. steel tubing with standard couplings is connected to the opening in the valve opposite the valve stem. One of the two hexagonal nuts on the couplings should be 2.3 instead of the usual 1 cm. in length.

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[1] Adkins, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 342 (1932). Unfortunately, mistakes were there made in the interconversion of inches and metric units, with respect to the thickness of the copper gasket (1.6 mm.), the internal chamber of the steel tubing (1.6 mm.), and the length of the spiral (4.3 m.).

TABLE I

DIMENSIONS OF BOMBS

		A		B	
		Inches	Cm.	Inches	Cm.
Bomb diameter	o. d.	2.12	5.40	2.31	5.88
	i. d.	0.75	1.90	1.31	3.34
Bomb length	o. d.	6.44	16.30	8.75	22.20
	i. d.	5.87	14.90	8.00	20.30
Thermocouple well	diam.	0.19	0.48	0.19	0.48
	depth	3.00	7.62	3.00	7.62
Bomb head	diam.	2.00	5.08	2.12	5.40
	thickness	0.50	1.27	0.50	1.27
Bomb head (boss)	diam.	.87	2.22	.87	2.22
	height	1.00	2.54	1.00	2.54
Channel in b. and b. h.	diam.	1.00	2.54	1.56	3.96
	depth	0.05	0.13	0.05	0.13
Gasket recess in b. h.[2]	depth	.15	.04	.15	.04
Bomb head cover	diam.	2.56	6.50	2.87	7.30
	height	2.62	6.66	2.75	7.00
Bomb head cover (recess)	diam.	2.03	5.13	2.15	5.45
	depth	1.87	4.76	2.00	5.08
Open. in b. h. cover for boss of b. h.	diam.	0.90	2.29	0.90	2.29
Threaded (8 per inch)	bomb	1.25	3.18	1.50	3.81
	b. h. c.	1.25	3.18	1.50	3.81
Copper gasket	o. d.	1.25	3.18	1.81	4.61
	i. d.	0.75	1.90	1.31	3.34
	thickness	.06	0.16	0.06	0.16
Brass thrust plate	o. d.	2.00	5.08	2.12	5.40
	i. d.	1.06	2.70	1.06	2.70
	thickness	0.12	0.32	0.12	0.32

(2) The i. d. diameter of the gasket recess should be the same as that of the gasket but the o. d. diameter should be somewhat greater than the o. d. diameter of the gasket in order to permit the expansion of the latter.

The bomb assembly consists of: a chamber, bomb head and bomb head cover, fabricated out of a roll (15 × 3 inches for bomb B) of annealed chrome vanadium steel, S. A. E. 6140, from the Crucible Steel Company, 17 East 42d Street, New York City; a copper gasket; a thrust plate; six $^7/_{16} \times 1^1/_4$ inch socket head cap screws of high tensile steel with 20 threads to the inch supplied by the Allen Manufacturing Company, Hartford, Connecticut; a 7.5 cm. length of 3 mm. copper tubing, for inlet of hydrogen, screwed into the hydrogen inlet on the lower face of the bomb head. A wrench to fit the standard coupling on the steel tubing and one to fit the cap screws and a small vise are necessary for opening and closing the bomb. The chamber should be protected from the pipe jaws of the vise by pieces of sheet copper.[3]

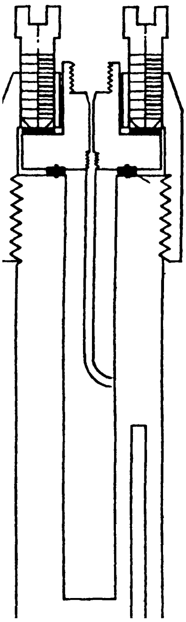

Fig. 1.—Cross section of bomb.

The procedure for standardizing the bomb is as follows. A standard solution of acetone or acetoacetic ester is made up of such a strength that 0.25 mole of the keto compound is contained in 100 ml. of an ethanol solution. Twenty ml. of the solution is placed in the chamber with 1 g. of copper–chromium oxide catalyst. The chamber is placed upright in the vise, the copper gasket placed in the gasket recess in the head, and the head put in position. The thrust plate is placed on the bomb head, and the bomb head cover screwed down to within a quarter of a turn as far as it will go. The cap screws are then turned down. The nipple (attached to the valve) is screwed into the bomb head. Care should be taken that the gage and the open end of the bent copper tube are so placed that both are pointing upward when the bomb assembly is later placed in the shaker. The bomb is then removed from the vise, and the valve connected to a hydrogen tank by the opening in the valve opposite the gage. Hydrogen is allowed to enter to the desired pressure. The valves on the tank and the bomb are closed and the bomb assembly detached from the connection to the tank. The bomb is then placed in the heater, mounted on a shaker, and the thermocouple put in place. After a few minutes of agitation of the contents of the bomb the pressure indicated on the gage will become constant if the connections are all tight. The procedure from this point on is essentially the same as that previously described.[1]

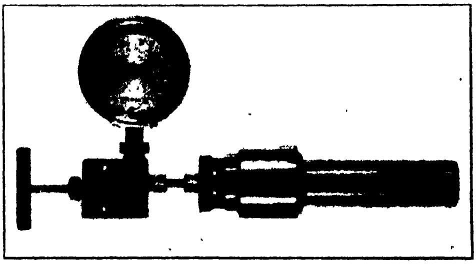

Fig. 2.—Apparatus for quantitative hydrogenation.

The temperature to be used is a function of the compound involved—150° for the hydrogenation of a ketone, and 250° for a carbethoxy group, for example. The heater for bomb (A) should contain about 30 feet of No. 22 nichrome wire in order to carry a current of about 3.7 amperes on 110 volts, while the heater for bomb (B) should have two coils connected in parallel, each 40 feet

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(3) The bombs described herewith were constructed by Mr. Lee Henke of this Laboratory.

in length. After reaction is complete the bomb may be removed immediately from the heater and allowed to cool to room temperature.

A number of compounds that are quantitatively hydrogenated may be used for purposes of standardization. The amount of compound used should be such as to bring about a drop in hydrogen pressure of 300 to 800 pounds. Ethanol or methylcyclohexane are suitable solvents for temperatures below 200°. Above that temperature butanol is more satisfactory in quantitative work, since its vapor pressure and coefficient of expansion are smaller. Nickel as well as copper-chromium oxide has been used as a catalyst.[4]

As a result of several determinations a pressure drop of 750 ± 10 pounds in bomb (A) was found to correspond to the hydrogenation of 0.05 mole of acetone or acetoacetic ester made up to 20 ml. This amount corresponds to a drop in pressure of 15,000 pounds per mole of hydrogen absorbed. The drop in pressure per mole of hydrogen is a function of the volume of hydrogen in the bomb so that with 10 instead of 20 ml. of liquid in the bomb, the drop in pressure per mole of hydrogen was found to be 10,500 to 10,800 (av. 10,700) pounds per mole in six determinations with acetone, acetoacetic ester, ethyl laurate and diethyl sebacate. The drop in pressure was 2800 pounds per mole of hydrogen for bomb B containing 50 ml. of liquid. The figures given are based upon pressure readings made while the temperature of the gas was approximately 23°.

In order to control the extent of hydrogenation it is important to be able to convert the pressure reading at the temperature of hydrogenation to the pressure reading at 23°. For this purpose the following figures, when used as divisors, have been found to give approximately the pressures at 23° in bomb A: 1.22 for 100°, 1.31 for 130°, 1.40 for 160°, 1.52 for 200° and 1.67 for 250°. These figures are less than would be calculated from the gas laws primarily because a portion of the hydrogen is in the Bourdon tube of the gage and consequently is not heated much above room temperature. They are not true for ethanol as a solvent at temperatures above 200°. The corresponding figures for bomb B may be calculated sufficiently accurately from the gas laws.

The tightness of the apparatus is indicated by the fact that bomb A containing hydrogen under a pressure of 100 atmospheres at 23° with butanol and copper-chromium oxide catalyst has been heated to 250° (167 atmospheres) and cooled to room temperature on five successive days without opening. At the end of the period the pressure registered by the gage was within 1 atmosphere of that originally observed. Thus the leakage, if any, of hydrogen from the bomb was less than 20 ml. of gas. The same gasket has been used almost daily for several weeks at 150 to 250° without a detectable leakage. The apparatus and procedures given above have been found repeatedly to give results which were reproducible within from 0.001 to 0.003 mole of hydrogen. Duplicate analyses made by Mr. Leo Kuick for ethyl nicotinate in a mixture with ethyl nipecotate over nickel at 165° showed 23.0 and 24.2% of the nicotinate for example.

Summary

Procedures and apparatus have been described which are useful for quantitative catalytic hydrogenations under pressures of 100 to 300 atmospheres.

MADISON, WISCONSIN

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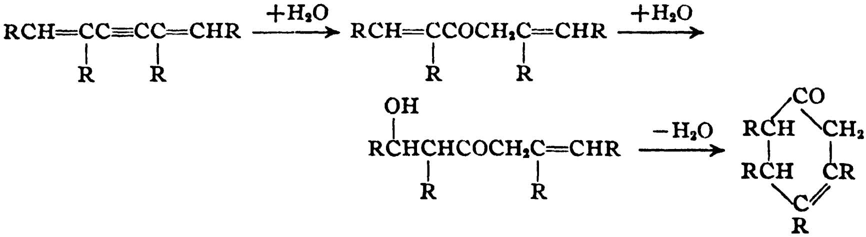
(4) If the bomb has not been used for several days, a film of oxide may form on the inside of the chamber so that it is advisable to make one or two preliminary hydrogenations at 250° before attempting quantitative work.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Cyclization of Substituted Divinylacetylenes

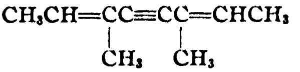
BY D. T. MITCHELL AND C. S. MARVEL

An investigation of the reactions of some substituted divinylacetylenes showed that treatment with sulfuric and acetic acids caused these dienines to undergo an unexpected hydration and cylization.[1] The following mechanism was proposed for the reaction:



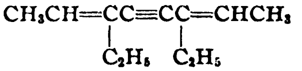
The oxidation and reduction products of the unsaturated ketone obtained from 4,7-di-*n*-propyldecadiene-3,7-ine-5 supported the cyclic structure which was assigned to it.

The unusual ring closure has now been observed in the case of two other tetrasubstituted divinylacetylenes, 3,6-dimethyloctadiene-2,6-ine-4 (I) and 3,6-diethyloctadiene-2,6-ine-4 (II). The cyclization of the tetramethyl derivative (I) could be accomplished only at low temperatures (0°). At room temperature only tarry polymerization products were produced. The dimethyldiethyl derivative (II) gave a good yield of cyclic ketone when the reaction was carried out at room temperature. No conditions were discovered which would enable us to apply this cyclization reaction to 2,5-dimethylhexadiene-1,5-ine-3 (III), although a wide range of temperature and acid concentration was tried. It is apparent that this cyclization reaction cannot be applied in a satisfactory manner to the disubstituted dienines where polymerization takes place rapidly.



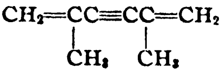
$CH_3CH{=}C(CH_3)C{\equiv}CC(CH_3){=}CHCH_3$

I



$CH_3CH{=}C(C_2H_5)C{\equiv}CC(C_2H_5){=}CHCH_3$

II



$CH_2{=}C(CH_3)C{\equiv}CC(CH_3){=}CH_2$

III

The mechanism which was previously proposed for the cyclization has been established by further experiments using 3,6-dimethyloctadiene-2,-6-ine-4 (I). The unsaturated ketone formed by the cyclization reaction has been shown to be 2,3,4,5-tetramethylcyclohexen-4-one-1 (IV) by ozonization which gave the known α,β-dimethyl-γ-ketovaleric acid (V) and by dehydrogenation to 2,3,4,5-tetramethylphenol (VI). Furthermore, the ketone was reduced to a hexahydroprehnitene (VII) which by dehydrogenation gave prehnitene (VIII).

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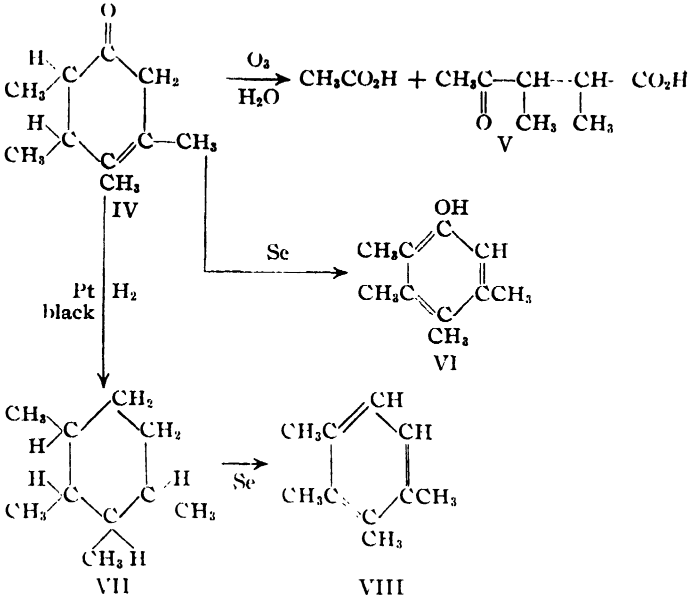
(1) Blomquist and Marvel, THIS JOURNAL, 55, 1655 (1933).



Experimental

Preparation of the Divinylacetylenes.—Tetramethylbutinediol, *sym*-dimethyldiethylbutinediol and tetraethylbutinediol were obtained in 70–90% yields as described by Dupont.[2] The dehydration of tetramethylbutinediol with sulfuric acid according to Dupont's[2] procedure was unsatisfactory. The best yields of 2,5-dimethylhexadiene-1,5-ine-3 were obtained by dehydrating the glycol with 60% phosphoric acid in an atmosphere of carbon dioxide. A solution of 25 g. of the glycol in 250 cc. of 60% phosphoric acid in a 500-cc. three-necked flask was distilled slowly. A fairly rapid current of carbon dioxide was passed through the boiling mixture and water was added from a dropping funnel to keep the concentration of the acid at about 60%. In about one-half hour the reaction was complete. The hydrocarbon was separated from the distillate, dried over magnesium sulfate and distilled under reduced pressure. The yield was 11–12 g. (60–70%) of a product boiling at 35° (5 mm.). Distillation at atmospheric pressure caused most of the hydrocarbon to polymerize.

The tetrasubstituted divinylacetylenes, 3,6-dimethyloctadiene-2,6-ine-4 and 3,6-diethyloctadiene-2,6-ine-4 were readily obtained in 75–85% yields by Dupont's procedure.[3] These hydrocarbons were more stable and did not polymerize so readily. The diethyl derivative has not been reported previously. It has the following properties: b. p. 80–81° (5 mm.); n^{20}_{D} 1.4965; d^{20}_{4} 0.8196.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.80; H, 11.19. Found: C, 89.00; H, 11.30.

This hydrocarbon was ozonized in carbon tetrachloride and the ozonide was decomposed with water. The α-ketobutyric acid was identified as the phenylhydrazone of m. p. 150°[3] and acetic acid was identified as the *p*-bromophenacyl ester, m. p. 84–85°.[4]

Preparation and Characterization of the Substituted Cyclohexenones.—The dienines were converted to the cyclic unsaturated ketones by the general procedure de-

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(2) Dupont, *Ann. chim.*, [8] **30**, 485 (1913).

(3) Barre, *Compt. rend.*, **184**, 825 (1927), gives this melting point at 152° on slow heating.

(4) Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920), give the melting point as 84–85°.

scribed in the previous paper.[1] Several variations of the experimental details were tried in the case of 2,5-dimethylhexadiene-1,5-ine-3 but only tarry products could be obtained. The cyclization of 3,6-dimethyloctadiene-2,6-ine-4 had to be carried out at 0° since at room temperature only tarry products were formed. The diethyl derivative reacted well at room temperature. The unsaturated ketones were characterized by preparing the 2,4-dinitrophenylhydrazones and by reduction to the saturated hydrocarbons by methods previously described in detail.[1] The new derivatives and their properties are given in Table I.

TABLE I

PROPERTIES OF SOME NEW CYCLOHEXANE DERIVATIVES

	Compound	Yield, %	B. p., °C. (mm.)	M. p., °C.
1	2,3,4,5-Tetramethylcyclohexene-4-one-1	25	84–86 (5)	.....
2	2,4-Dinitrophenylhydrazone	..	.....	158–159
3	1,2,3,4-Tetramethylcyclohexane	85	84 (5)	.....
4	3,4-Dimethyl-2,5-diethylcyclohexene-4-one-1	36	104–107 (5)	.....
5	2,4-Dinitrophenylhydrazone	..	.....	138–139
6	1,2-Dimethyl-3,6-diethylcyclohexane	75	91–92 (4)	.....

				Analyses, %			
				Carbon		Hydrogen	
	n_D^{20}	d_4^{20}	Formula	Calcd.	Found	Calcd.	Found
1	1.4690	0.9298	$C_{10}H_{16}O$	78.87	78.90	10.60	10.75
2	....	....	$C_{16}H_{20}N_4O_4$	N, 16.86; found, 17.03			
3	1.4531	.8219	$C_{10}H_{20}$	85.62	85.73	14.38	14.54
4	1.4820	.9152	$C_{12}H_{22}O$	79.93	79.82	11.19	11.15
5	....	....	$C_{18}H_{24}N_4O_4$	N, 15.50; found, 15.69			
6	1.4673	.8536	$C_{12}H_{24}$	85.62	85.70	14.38	14.47

Ozonization of 2,3,4,5-Tetramethylcyclohexene-4-one-1.—This ozonization and the subsequent hydrolysis were carried out by the procedures described before.[1] The acid volatile with steam was identified as acetic acid by converting it to the *p*-bromophenacyl ester, m. p. 84–85°.[4] The non-volatile acid boiled at 120° (5 mm.) and was identified as α,β-dimethyl-γ-ketovaleric acid.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.29; H, 8.33; neutral equivalent, 144.1. Found: C, 58.41; H, 8.42; neutral equivalent, 142.0.

The *p*-nitrophenylhydrazone was prepared and found to melt at 123°. This derivative has previously been recorded as melting at 121–123°.[5]

Dehydrogenation of 1,2,3,4-Tetramethylcyclohexane.—Two grams of this hydrocarbon was dropped onto powdered selenium previously heated to about 400°. The distillate was condensed and combined with an ether extract of the cooled selenium. The extract was washed with water, dried over magnesium sulfate, filtered and distilled. A fraction was collected from 190–210° and then carefully refractionated. The product weighed 0.75 g., b. p. 202–203° (745 mm.); n_D^{20} 1.5211; d_4^{20} 0.9017. A sample of prehnitene[6] had the following constants; b. p. 203° (760 mm.); n_D^{20} 1.5203; d_4^{20} 0.9010.

Dehydrogenation of 2,3,4,5-Tetramethylcyclohexene-4-one-1.—Ten grams of this ketone was dehydrogenated by the procedure described for the hydrocarbon. The ether solution of the crude distillate was extracted with 5% sodium hydroxide solution. The alkaline solution was separated and acidified. The phenol which separated was collected in ether, the ether was evaporated and the residue was recrystallized from benzene. About 0.1 g. of a product of m. p. 80° was obtained. The melting point of this product was not depressed by mixing it with a sample of 2,3,4,5-tetramethylphenol prepared from prehnitene.[7] Limpach gives the melting point of this phenol as 80–81°.[8]

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(5) Willstätter and Brossa, *Ber.*, **44**, 2192 (1911).

(6) We are greatly indebted to Professor Lee Irvin Smith for the prehnitene which was used for this experiment and for the preparation of 2,3,4,5-tetramethylphenol.

Summary

1. The cyclization of substituted divinylacetylenes has been extended to 3,6-dimethyloctadiene-2,6-ine-4 and 3,6-diethyloctadiene-2,6-ine-4. The reaction could not be applied to the disubstituted divinylacetylene, 2,5-dimethylhexadiene-1,5-ine-3.

2. The structure proposed for the ring compounds and the mechanism of the cyclization reaction have been established by converting the cyclohexane derivatives obtained from 3,6-dimethyloctadiene-2,6-ine-4 to known derivatives of tetramethylbenzene.

[7] Cummings, Hopper and Wheeler, "Systematic Organic Chemistry," Constable and Co., London, 1931, pp. 323, 210.

[8] Limpach, *Ber.*, **21**, 645 (1888).

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Dehalogenation of Aliphatic Bromo Acids. The Bromo and Dibromo Olefins*

BY G. BRYANT BACHMAN

Dehalogenation of cinnamic acid dibromide may lead to the formation of cinnamic acid, α-bromocinnamic acid, α-bromoallocinnamic acid or ω-bromostyrene or mixtures of all of these depending upon the conditions of dehalogenation and particularly on the nature of the dehalogenating base used. In the aliphatic series the dehalogenation of α,β-dibromo acids has been less thoroughly studied and although the bromoolefins analogous to ω-bromostyrene have been detected among the products in some cases, attention has generally been centered on the relative yields of α-bromo and α-bromoisoolefinic acids. No systematic efforts have been made to isolate the 1-bromo-1-olefins formed and determine their physical and chemical properties and their yields.

There are apparently two other well-defined methods available for the preparation of 1-bromo-1-olefins (1) the dehalogenation of olefin dibromides

$$2RCHBrCH_2Br + \text{Alc. KOH} \longrightarrow \begin{matrix} RCH{=}CHBr \\ +RCBr{=}CH_2 \end{matrix} + 2KBr + 2H_2O \qquad (1)$$

and (2) a method recently devised by Kirrmann.[1] Neither of these methods is entirely satisfactory—the first yielding a mixture of isomers which is difficult to separate completely into the pure components and the second being rather roundabout and applicable only with difficulty to some members of the series. In view of the fact that these bromoolefins might be expected to serve as unexcelled intermediates for the preparation of normal acetylenes, it seemed desirable to study their formation through the decomposition of a series of aliphatic olefinic acid dibromides.

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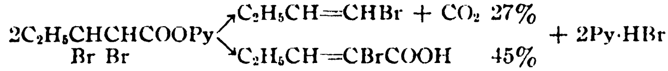
* Presented before the Organic Section at the Chicago Meeting of the American Chemical Society, September, 1933.

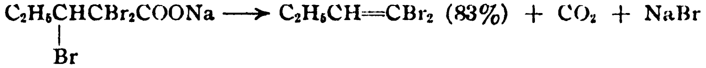
[1] Kirrmann, *Bull. soc. chim.*, **41**, 316–323 (1926).

It has been found that the organic as well as the inorganic salts of the α,β-dibromo acids from butyric acid through pelargonic acid decompose when heated to give 1-bromo-1-olefins in from 20 to 35% yields depending among other things on the base used. Thus when α,β-dibromovaleric acid dissolved in pyridine is heated the following reactions occur



$$\underset{\text{Br}\ \ \text{Br}}{2C_2H_5CHCHCOOPy} \begin{array}{l} \nearrow C_2H_5CH{=}CHBr + CO_2 \ \ 27\% \\ \searrow C_2H_5CH{=}CBrCOOH \ \ 45\% \end{array} + 2Py{\cdot}HBr \qquad (2)$$

The 1-bromo-1-olefins thus formed, when isolated, are exceptionally pure, colorless, pleasant odored liquids, and are uncontaminated with the isomeric 2-bromo-1-olefins or more highly brominated products. The above decomposition may be explained most simply perhaps on the assumption that there are two simultaneous competitive reactions occurring, the more rapid one being a simple dehalogenation in which the β-bromine atom and the α-hydrogen atom are removed together with the resulting formation of an α-bromoolefinic acid, the second reaction giving rise to the bromoolefin.[2] In the aromatic series, *i. e.*, when the β-carbon is substituted by a phenyl group, this latter reaction predominates. In the aliphatic series, however, it is subordinate. The nature of the substituent groups therefore exerts a marked influence on the relative rates of these two reactions. This would lead one to predict that even higher yields of bromoolefins would result from the decomposition of acids containing a still greater number of electronegative atoms or groups. This was found to be the case—the α,α,β-tribromo acids decompose to give 1,1-dibromo-1-olefins in excellent yields.



$$C_2H_5\underset{\substack{|\\ Br}}{CH}CBr_2COONa \longrightarrow C_2H_5CH{=}CBr_2\ (83\%) + CO_2 + NaBr \qquad (3)$$

It should also be pointed out, of course, that here a simple dehalogenation reaction of the previously illustrated type is impossible since there is no α-hydrogen atom available. Without competition from this reaction then the formation of the dibromoolefin proceeds practically completely. Beta-gamma dehalogenation does not seem to occur to an appreciable extent.

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(2) Two different mechanisms have been proposed to account for this second type of reaction The earlier one of Erlenmeyer, *Ber.*, **13**, 303 (1880), assumes the intermediate formation of β-lactones More recently Johansson, *ibid.*, **48**, 1262 (1915), and **55**, 647 (1922), proposes the simultaneous elimination of carbon dioxide and the bromide ion. Further research is in progress to determine which of these mechanisms explains most satisfactorily the present work.

Of the 1,1-dibromo-1-olefins only 1,1-dibromo-1-propene has been mentioned previously in the literature.[3] Unfortunately it was inadequately described. The compounds prepared by the writer were found to be colorless, pleasant odored, mobile but dense liquids, which on standing in the air absorbed oxygen and took on an acid bromide odor. 1,1-Dibromo-1-propene absorbed oxygen especially quickly and had a pungent odor within fifteen minutes after preparation. Sealed tubes containing this compound were found to be under diminished pressure after standing for only a week. This reaction is being further investigated for comparison with the oxidation of 1,1-dibromoethylene by atmospheric oxygen.[4] If the reactions are analogous, α-bromopropionyl bromide should result

$$2CH_3CH{=}CBr_2 + O_2 \longrightarrow 2CH_3CHBrCOBr \qquad (4)$$

The series of α-bromoolefinic acids formed by reaction (2) and the α,α,β-tribromo acids prepared by their bromination are new except α-bromocrotonic and α,α,β-tribromobutyric acids. Although several different kinds of salts of α,β-dibromo acids were decomposed, the pyridine salts were found to be most satisfactory since the α-bromo acids resulting were purer and furthermore were not contaminated with the corresponding α-bromo iso acids or bromohydroxy acids.[5] Dehalogenation of the α,β,β-tribromo acids was accomplished more conveniently with dilute sodium carbonate solution since side reactions were found to be inconsiderable, and practically the only products were dibromoolefins.

Experimental Part

Olefinic Acids.—These acids were prepared in excellent yields by the condensation of the appropriate aldehydes with malonic acid in the presence of pyridine.[6] Hexaldehyde was prepared in 60% yields by the reaction of 1 mole of *n*-amylmagnesium bromide with 1 mole of orthoformic ester, a method apparently not hitherto used for its preparation. The following constants were obtained: b. p. (747 mm.), 126–128°; n^{20}_{D} 1.4068; d^{20}_{4} 0.8176. Several unsuccessful attempts were made to dehydrogenate *n*-hexyl alcohol with metallic copper according to the procedure of Sabatier and Mailhe. Although some aldehyde was formed, its preparation by this method was found to be impracticable. The catalytic oxidation of alcohols in the presence of copper bronze and nitrobenzene recommended by Rosenmund[7] was also tried. It proceeded too slowly to be of value when considerable quantities of hexaldehyde were desired

Of the olefinic acids α-octenic acid is new. The following constants were noted. b. p. (22 mm.) 154° (corr.); n^{20}_{D} 1.4587; d^{20}_{4} 0.9807. The acid was analyzed in the form of its *p*-bromophenacyl ester, m. p. 92.5°.

Anal. Calcd. for $C_{16}H_{19}O_3Br$: Br, 23.6. Found: Br, 23.4, 23.5.

α,β-Dibromo Acids.—The carefully fractionated olefinic acids were brominated in carbon disulfide with a small excess of bromine at 5°. Direct sunlight has a most marked influence on the speed of this reaction. On dull days several hours are required for completion of a bromination that is completed within twenty minutes when the sun is shining directly on the reaction flask. The α,β-dibromo acids used in this investigation have all been described except α,β-dibromoheptanoic and α,β-dibromooctanoic acids.

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[3] Valentin, *Ber.*, **28**, 2664 (1895).

[4] Demole, *ibid.*, **11**, 316 (1878).

[5] Pfeiffer, *ibid.*, **43**, 3039 (1910).

[6] Auwers, *Ann.*, **432**, 46 (1923).

[7] Rosenmund, *Ber.*, **54**, 2033 (1921).

Acid	M. p., °C.	Analyses for bromine, % Calcd.	Found	
$C_4H_9CHBrCHBrCOOH$	74.5	55.5	55.2	55.2
$C_5H_{11}CHBrCHBrCOOH$	Oil	53.0	53.6	53.4
$C_6H_{13}CHBrCHBrCOOH$	44	50.6	50.9	50.8

The reported melting point of α,β-dibromononanoic acid is 35°.[8]

The 1-Bromoolefins.—If the above α,β-dibromo acids are treated with an equivalent amount of dilute (5 or 10%) sodium carbonate the solutions formed appear to be stable at room temperatures for several days. If heated, however, they evolve carbon dioxide, become turbid and rapidly separate an oily layer, which partially distils with the steam when the mixture is boiled. Similar results were obtained by heating the ammonium, pyridinium, silver and potassium salts in aqueous solution. The table shows the comparative percentage yields of 1-bromo-1-octene from α,β-dibromopelargonic acid.

Salt	K	Na	Py	NH_4	Ag
Yield, %	30	30	26	20	20

With anhydrous pyridine dried and fractionated over barium oxide a different procedure was necessary. One mole of acid was dissolved in 3 moles of pyridine and the solution heated on the steam-bath. Within one-half hour a separation of pyridine hydrobromide occurred with an accompanying darkening of the solution and an evolution of carbon dioxide. Heating was continued for three hours, the brown solution cooled and poured into an excess of concentrated hydrochloric acid mixed with an equal weight of crushed ice. The lower oily layer was separated and distilled with water. The bromoolefins distil rapidly with the first few cubic centimeters of water. After drying over calcium chloride they are nearly pure and boil almost completely within a two degree range.

1-BROMOOLEFINS

	Yield, %	B. p., °C. (corr.)	Press., mm.	d^{20}_{20}	n^{20}_{D}	Analyses for bromine, % Calcd.	Found	
1-Propene[a]	28	58–60	747	1.4181	1.4560	66.1	65.9	65.7
1-Butene[b]	28	87–89	747	1.3123	1.4536	59.3	59.0	59.1
1-Pentene[c]	32	113–115	747	1.2391	1.4572	53.7	53.3	53.5
1-Hexene[d,e]	27	138–140	747	1.1910	1.4584	49.1	49.0	48.7
1-Heptene[c,d]	35	161–163	747	1.1553	1.4594	45.2	44.7	44.8
1-Octene[f]	26	178–180	750	1.1342	1.4602	41.9	41.7	41.7

[a] "Int. Crit. Tables," Vol. I, p. 182. [b] Lépingle, *Bull. soc. chim.*, **39**, 748 (1926). [c] Kirrmann, *ibid.*, **41**, 316 (1926). [d] Welt, *Ber.*, **30**, 1494 (1897). [e] Hecht and Strauss, *Ann.*, **172**, 70 (1874). [f] Rubien, *ibid.*, **142**, 298 (1867).

1-Bromo-1-octene gave a 70% yield of 1-octine, b. p. 123–126°, on dehalogenation with potassium hydroxide and mineral oil at 175°. The monobromoolefins react readily with one mole of bromine in carbon disulfide to yield colorless tribromides having a mild camphor-like odor. These products were not further investigated.

An attempt was made to prepare pure 1-bromo-1-octene through dehalogenation of 1,2-dibromooctane. A small sample of very pure 1-octene[9] was brominated in carbon disulfide at 0°. After isolation and purification the 1,2-bromooctane had the constants

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(8) Harding and Weizmann, *J. Chem. Soc.*, **97**, 301 (1910).

(9) Kindly supplied by Professor C. E. Boord of this institution.

b. p. (12 mm.) 117°; n^{20}_D 1.4942. It was recovered unchanged after boiling for three hours with pure dry pyridine or with an ethyl alcohol solution of pyridine. With alcoholic potassium hydroxide a mixture was obtained which on account of the small amount available could not be separated completely into its components. The liquid gave a test for an acetylene (octine) with alcoholic silver nitrate and contained some 1-bromo-1-octene as well as 2-bromo-1-octene and a vinyl ether, all of which products are known to result from this type of reaction.

Alpha Bromo Acids.—The oils remaining after removal of the bromoolefins and acidification were separated and distilled under diminished pressure except in the case of the first member of the series. α-Bromocrotonic acid is soluble in water. It was therefore extracted with ether and recrystallized from hot water. Of the remaining acids those which were solid at room temperatures were recrystallized from petroleum ether.

α-BROMOOLEFINIC ACIDS

	M. p., °C.	B. p., °C.	Press., mm.	Analyses for bromine, % Calcd.	Found		Yield, %
Crotonic	106–107						55
α-Pentenoic	49–50	122–124	15	44.7	44.4	44.5	45
α-Hexenoic	37–38	143–145	15	41.4	41.3	41.2	40
α-Heptenoic	Oil	153–156	15	38.6	38.6	38.7	38
α-Octenoic	Oil	165–167	15	36.2	36.0	35.8	40
α-Nonenoic	Oil	176–179	15	34.0	33.5	33.4	35

α,α,β-Tribromo Acids.—The carbon disulfide solutions of the α-bromoolefinic acids readily absorbed one mole of bromine in the presence of direct sunlight to give practically quantitative yields of the corresponding tribromo acids. Less heat was evolved than in the bromination of the olefinic acids. The products except the eight and nine carbon atom acids formed masses of large hard white crystals upon evaporation of the solvent. After one recrystallization from petroleum ether they were pure. The oily tribromocaprylic and tribromopelargonic acids were left in a vacuum desiccator over solid potassium hydroxide for several days before analyzing.

α,α,β-TRIBROMO ACIDS

	M. p., °C.	Analyses for bromine, % Calcd.	Found	
Butyric	117.5			
Valeric	90.5–91	70.8	70.7	70.6
Caproic	102.5	68.0	67.7	67.8
Enanthic	72	65.4	65.4	65.3
Caprylic	Oil	63.0	63.3	63.2
Pelargonic	Oil	60.8	60.8	60.6

1,1-Dibromoolefins.—The tribromo acids were dissolved in a small excess of dilute aqueous sodium carbonate and the solutions heated to boiling. Turbidity appeared,

1,1-DIBROMOOLEFINS

	Yield, %	B. p., °C.	Press., mm.	d^{20}_{20}	n^{20}_D	Analyses for bromine, % Calcd.	Found	
1-Propene[a]	88	127.4	750	1.9803	1.5260	80.0	79.6	79.8
1-Butene	83	53–55	22	1.8348	1.5168	74.8	74.4	74.6
1-Pentene	79	72–74	22	1.7013	1.5097	70.2	69.8	69.7
1-Hexene	75	90–92	22	1.6047	1.5050	66.1	65.9	65.7
1-Heptene	74	105–107	22	1.5130	1.5009	62.5	62.2	62.3
1-Octene	70	120–122	22	1.4448	1.4978	59.3	59.0	58.9

[a] Valentin, *Ber.*, **28**, 2664 (1895).

carbon dioxide was evolved and oily layers formed which distilled with the water vapor. The products were dried over calcium chloride and distilled. The decreased yields found among the higher members of the series as indicated in the table below are probably the result of partial hydrolysis by water. Longer heating with water is necessary to steam distil these higher boiling substances than is necessary with the members of lower molecular weight.

With bromine the 1,1-dibromoolefins form tetrabromides which are colorless oils and which have an intense camphor-like odor. These products were not further investigated.

Summary

The decompositions of α,β-dibromo and α,α,β-tribromo aliphatic acids with alkaline reagents yield the corresponding 1-bromoolefins and α-bromoolefinic acids in the first case and 1,1-dibromoolefins in the second case.

The 1-bromo-1-olefins may serve as intermediates in the preparation of normal acetylenes in good yields. The 1-bromoolefins as well as the 1,1-dibromoolefins add one mole of bromine to yield oils having camphor-like odors.

COLUMBUS, OHIO RECEIVED JUNE 19, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Phosphoric Acid in Organic Reactions

BY WILLIAM M. DEHN AND KIRBY E. JACKSON

Phosphoric acid is superior to sulfuric acid as a catalyst in certain organic reactions of hydrolysis,[1] dehydration and isomerization Its chief advantages are disclosed in its lesser tendency to carbonize or otherwise to react with the organic materials, hence these processes can be made to deliver larger yields of desired products. Furthermore, the phosphoric acid can be recovered from the reaction mixtures practically pure for repeated use.

We have found that it is the ideal catalyst for ketonic hydrolyses of alkyl acetoacetates, having obtained 95% yields of the ketones and no fatty acids, whereas sulfuric acid and the alkalies give less than 70% yields of the ketones. The advantages here result from lesser carbonization, from lesser quantities of water used, and in the simple method of reprocessing fractions containing unchanged acetoacetates. Because either acids or alkalies hydrolyze the acetoacetates, the mechanism of reaction seems to be conditioned by the capacity of the reagent to add to the reactant before hydrolysis results.

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(1) For the use of phosphoric acid to prepare olefins, see Newth, *J. Chem. Soc.*, **79**, 915 (1901); Adams, Kamm and Marvel, THIS JOURNAL, **40**, 1951 (1918); German Patent 66,866.

Cyclohexanol, menthol and certain hydroxylated terpene derivatives were practically quantitatively dehydrated by phosphoric acid. It isomerized pinene to dipentene and terpinene, and gave dipentene, terpinolene and terpinene as the chief products from terpin hydrate, terpineol[2] and cineol. Also it polymerized pinene and other terpenes. In all cases, the concentration of the acid and a high temperature were the important conditions to effect either dehydration or isomerization, otherwise quite different products were formed.

As a qualitative reagent, for example, in testing for cocaine and other benzoylated derivatives, the acid gave positive indications with minute quantities of material tested. The acid was found to be useful for the identification of carbohydrates[3] and glucosides.

Experimental

In the following experiments phosphoric acid of 85% concentration was used. For recovery of the acid, the residual mixture was diluted with water and filtered. If too dark in color, this was concentrated by evaporating with a little nitric acid to sp. gr. 1.70.

Ketonic Hydrolysis of Ethyl *n*-Amylacetoacetate.—A mixture of 200 g. of acid and 200 g. of the acetoacetate was placed in a one-liter round-bottomed flask which carried a dropping funnel and was attached to a condenser. Moderate heating in an oil-bath caused evolution of carbon dioxide and the distillation of an oil–water mixture. From time to time this distillate was placed in the dropping funnel and the lower aqueous layer was permitted to drop into the flask as the distillation continued. Later the oily layer was fractionated through a column and the oil boiling above 155° was returned to the flask for further hydrolysis. By repetition of these processes and with effective fractionation of the oils, 95% yields of methyl amyl ketone boiling at 150–150° were obtained. The alcohol fraction must be salted out with calcium chloride to obtain the maximum yield of the ketone.

Because ketones give high boiling chain condensation products by treatment with the acid at high temperatures, the above reaction should be carried on so as to avoid the evolution of white cloudy vapors.

It was thought that if the concentration of the hydroxyl ions was kept low, large yields of the ketone could be obtained with alkalies. Employing essentially the method of Johnson and Hager[4] barium and calcium hydroxides were tried. With 0.2–1.0 mole of barium hydroxide, all added at once or aliquot parts added during four hour periods the yields were 40–60%. With 1.3–2.7 moles of calcium hydroxide, all added at once, the yields were 60–70%. Thus though the yields with calcium hydroxide were better, in no case of nine experiments could the yields be raised above 70%. Owing to the large quantities of water used, and otherwise, this method is laborious and is greatly inferior to the phosphoric acid method.

Cyclohexene from Cyclohexanol.[5]—A one-liter round-bottomed flask, containing 100 g. of acid and carrying both a dropping funnel and a distilling column attached to a condenser, was heated in an oil-bath at 160–170°. Through the funnel 500 g. of pure cyclohexanol was dropped in at such a rate as was convenient to collect the distillate, whose receiver was surrounded by ice water. During the distillation, a thermometer in

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(2) Wallace [*Ann.*, **275**, 106 (1893)] reports that 20% acid only slowly yields terpinine, terpinoline and cineol.

(3) Dehn, Jackson and Ballard, *Ind. Eng. Chem., Anal. Ed.*, **4**, 413 (1932).

(4) "Organic Syntheses," Coll. Vol. I, 1932, p. 343.

(5) For comparative methods, see "Organic Syntheses," Coll. Vol. I, 1932, p. 177.

the column registered temperatures below 100°. The distillate separated into oily and aqueous layers. The upper layer was dried with calcium chloride and then fractionated through an efficient column, taking only that which came over below 88°. The residual oil and the original aqueous layer were returned to the reaction flask for further dehydration and distillation. By repetition of these processes, ultimately 393 g. of oil boiling below 88°, or 96% of cyclohexene, was obtained. The residual oil (19 g.) yielded unchanged cyclohexanol and a higher boiling oil (200–230°) which will be investigated.

Menthene from Menthol.—A mixture of 100 g. of menthol and 50 g. of phosphoric acid was heated in a round-bottomed flask under a reflux condenser for four hours, and then the contents were distilled up to 200°. The oily layer was separated, dried with calcium chloride and distilled. The fraction boiling at 166–170° weighed 82 g., which is equal to a 94% yield of menthene.

Dehydration of Terpin Hydrate.—The reactions here are dehydration, isomerization and polymerization. A mixture of 100 g. of acid and about 200 g. of terpin hydrate was distilled from a flask heated to 200° in an oil-bath, then other similar portions of 970 g. of the hydrate were added and distilled. Finally the water of the distillate was dropped in as long as oily distillate passed over. The theoretical yield[6] of dehydrated oil was 694 g.; found 685 g. Its repeated fractionation[7] gave 65% boiling at 172–777° (dipentene); 18% boiling at 177–181° (terpinene); 2% boiling at 181–190° (terpinoline) and 11% boiling at 315–325° (colophene). A dehydration of 500 g. of terpinene hydrate at 150–160° gave 98% of oil, 50% of which boiled within the range of terpinene and only 2–3% was colophene.

Isomerization of Turpentine.—When turpentine was dropped into 40–60% acid at 200° only 10–20% was isomerized or polymerized. When 436 g. was dropped into 98–100% acid at 200° more than 95% was transformed, 430 g. being separated and fractionated as follows; 3% boiling below 170°; 72% boiling at 170–177°; 3% boiling at 177–190°; 16% boiling to 325°, mostly colophene.

Terbene.—Medicinal terbene, which fractionated 75% below 165°, was reprocessed as with turpentine and then gave 90% boiling above 170°.

Dehydration of Terpineol.—When 100 g. of practical terpineol and 50 g. of acid were refluxed for four hours, the oil was separated and fractionated as follows: 8% boiling up to 173°; 54% boiling at 173–177°; 15% boiling at 177–183°; 2% boiling at 183–187°; 16% above 187°.

Dehydration of Cineol.—When 100 g. of cineol and 50 g. of acid were mixed, heat developed and a white solid[8] separated. This solid dissolves on heating. After refluxing for four hours, the oil gave the following fractions: 8% below 173°; 54%, 173–177°; 19%, 177–183°; 15% above 183°.

Pinacol Hydrate.—When 100 g. of pinacol hydrate and 50 g. of acid were refluxed for four hours and then distilled to 180°, refractionation gave: 3.8% below 80° (2,3-dimethylbutadiene); 7.8%, 80–90°; 5.7%, 90–100°; 70%, 100–110° (pinacoline); 10% 110–150° (dimethylisopropenylcarbinol).

Condensation of Acetone.—When equal weights of phosphoric acid and acetone are mixed, heat is developed; on distilling, fractions boiling up to 200° are obtained. When the lower fractions were dropped into the residue of phosphoric acid heated to high temperatures, heavy white smoke was evolved and the distillate yielded fluorescent

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(6) In this paper the percentages of fractions obtained were calculated on the basis of the theoretical yields.

(7) Waletzky acted on terpene hydrate at 50–80° with anhydrous phosphoric acid and reported the formation of terpinine, *Compt. rend.*, **94**, 90 (1882).

(8) Baeyer and Villiger, *Ber.*, **35**, 1206 (1902). Terpinine, terpinolene, dipentene and dicinene [Hell and Stürche, *ibid.*, **17**, 197 (1884)] have been reported as dehydration products.

oils boiling all the way up to 350° and a residue of carbon was found in the acid. These chain condensation products will be studied.

Qualitative Tests.—Numerous compounds have been identified by the use of sulfuric acid, which may give colors, liberate odorous components or yield sublimates. Since it may sulfonate, oxidize or char various compounds, it was thought that substitution of it by phosphoric acid would give better tests for certain compounds. This substitution has been made before for a few color reactions[9] and odors.[10]

Whereas cocaine has been identified[11] through its hydrolysis by sulfuric acid to benzoic acid, the following test is more convenient. In a clean, dry vial is placed some of the material, suspected to contain cocaine, to this is added 2–3 cc. of 85% phosphoric acid and the mixture is slowly heated on a hot-plate. If cocaine is present, needles of benzoic acid are sublimed to the upper part of the vial.

When material for melting point determinations is desired, longer heating is necessary. The bottom of a small crucible, covered with a thin layer of the solid, or 1–2 cc. of the liquid, to be examined, is treated with 2–3 cc. of phosphoric acid. The crucible, covered with a watch glass, is heated and, if a volatile acid is a product of the hydrolysis, it is obtained as a sublimate and its melting point can be taken. In case the substance under examination is a liquid requiring heating for a longer time, as is the case with methyl salicylate, a few cubic centimeters of water can be placed in the concave surface of the watch glass, to facilitate the collection of the sublimate.

The following substances easily gave benzoic acid with approximately correct melting point: alypin, benzaminoacetic acid, benzyl benzoate, butyl benzoate, cocaine, ethyl benzoate, ethyl hippurate, beta-eucaine, methyl benzoate, stovaine, tropacocaine.

The following substances easily gave salicylic acid with approximately correct melting point: aspirin, *o*-hydroxybenzoic acid, methyl salicylate, salol.

Summary

As a hydrolyzing agent, phosphoric acid gives superior yields of ketones from acetoacetates. As a dehydrating agent, it gives nearly quantitative yields of hydrocarbons from certain oxygenated terpines, and pinacol hydrate. It isomerizes pinene to mixtures of monocyclic terpenes. It condenses terpenes to colophene and acetone to high boiling chain compounds. It is a convenient qualitative reagent to liberate benzoic and salicylic acids from their derivatives.

SEATTLE, WASHINGTON

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(9) Alkaloids: Arnold, *Z. anal. Chem.*, **23**, 229 (1874); Palet, *J. pharm. chim.*, **19**, 295 (1919); Gallic acid: Drechsel, *J. prakt. Chem.*, **24**, 44 (1881); **27**, 424 (1883); Digitalin: Fluckiger, *Jahresber; Pharm.*, [3] **24**, 459.

(10) Atropine: Nowak and Kratschmer, *Med. chim.*, 276 (1895).

(11) Biel, *Pharm. Z.*, **31**, 132; Aurelj, *Giorn. farm. chim.*, **53**, 385; Scharges, *Z. anal. Chem.*, **36**, 541.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Behavior of Piperonal Derivatives toward Bromination and Nitration[1]

BY L. CHAS. RAIFORD AND FRED W. OBERST

This work was done in an effort to obtain polybromo and polynitro compounds from piperonal for use in testing the effect of negative substituents in the formation of stereoisomeric benzaldoxime derivatives.[2] Previously Orr, Robinson and Williams,[3] and later Parijs,[4] found that treatment of an acetic acid solution of piperonal with bromine gave a mixture of 6-bromopiperonal and 4,5-dibromocatechol methylene ether, which involved the replacement of the aldehyde group by halogen. When a sodium carbonate solution of piperonylic acid was treated with bromine water, only the dibromo ether was obtained.[5]

In the present work 6-bromopiperonal was treated with excess of bromine in the presence of aluminum bromide[6] at about 100°. When sodium acetate was present tetrabromocatechol methylene ether was isolated; in the absence of the acetate nearly all the ether was split to give tetrabromocatechol.[7] In both cases the aldehyde group was replaced by bromine.

Attempts were next made to protect the aldehyde group. The sodium bisulfite addition product[8] of piperonal and the corresponding 6-bromo compound gave, when brominated as indicated above, tetrabromocatechol methylene ether. When the diacetate was used[9] similar results were obtained.

Since 6-bromopiperonal could not be further brominated without loss of the aldehyde group, it was of interest to try to nitrate it. The product obtained by Fittig and Mielch[10] by the action of fuming nitric acid on 6-bromopiperonal, and recorded by Oelker[11] as a bromodinitropiperonal, was studied by Jones and Robinson,[12] who regarded it as a bromodinitrocatechol methylene ether, formed by the loss of the aldehyde group during nitration. Reduction of this product by stannous chloride and hydrochloric acid[13] caused the loss of bromine and gave a diamino

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(1) From a portion of the thesis submitted by F. W. Oberst in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Iowa, 1930.

(2) Brady and Dunn, *J. Chem. Soc.*, **107**, 1858 (1915).

(3) Orr, Robinson and Williams, *ibid.*, **111**, 947 (1917).

(4) Parijs, *Rec. trav. chim.*, **49**, 28 (1930).

(5) Jones and Robinson, *J. Chem. Soc.*, **111**, 913 (1917).

(6) Prepared as directed by Bodroux [*Compt. rend.*, **126**, 1282 (1898)].

(7) Raiford and Howland, THIS JOURNAL, **53**, 1051 (1931).

(8) Raiford and Stoesser [*ibid.*, **50**, 2560 (1928)] used bisulfite to protect the aldehyde group in 2,5-dibromovanillin.

(9) Raiford and Lichty, *ibid.*, **52**, 4577 (1930).

(10) Fittig and Mielch, *Ann.*, **152**, 50 (1869).

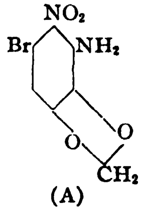
(11) Oelker, *Ber.*, **24**, 2594 (1891).

(12) Jones and Robinson, *J. Chem. Soc.*, **111**, 908, 919 (1917).

(13) Ref. 12, p. 927.

compound that the authors did not isolate but which was condensed immediately with phenanthrenequinone, thus indicating the *ortho* relations of the nitro groups[14] in the parent substance.

In the present work treatment of this bromodinitromethylene ether with ferrous hydroxide[15] gave the corresponding diamino compound without loss of bromine, and the product was isolated and characterized. When reduction was carried out with ammonium sulfide only one nitro radical was reduced to give an aminonitrobromo derivative which probably has the structure given (A). Support for this view was obtained by the behavior of the product when subjected to the indophenol test described by Autenrieth.[16]



(A)

A second point of interest was the study of other methods which it was hoped might give a bromonitropiperonal. Protection of the aldehyde radical, as indicated above for bromination, was unsuccessful. Treatment of the diacetate, and of the oxime of 6-bromopiperonal, respectively, with fuming nitric acid at 0° gave the bromodinitrocatechol methylene ether previously indicated, and when more dilute acid was used no reaction occurred. Parijs[17] found that treatment of an acetic anhydride solution of 6-bromopiperonal diacetate with "absolute nitric acid" split the methylene oxide ring and gave 6-bromoprotocatechuic aldehyde. Repetition of this experiment with fuming nitric acid, in the present work, caused loss of the aldehyde group, the opening of the methylene oxide ring and the formation of 3,4-dihydroxy-6-bromonitrobenzene. When nitric acid of lower concentration was used no reaction occurred.

The changes indicated above are shown in the accompanying diagram.

Experimental Part

Tetrabromocatechol Methylene Ether.—To 5 g. of 6-bromopiperonal in a 1-liter flask attached by a ground glass joint to a return condenser there was added an excess of bromine containing about 1% of aluminum bromide, and the mixture heated in an oil-bath at about 100° for three hours.[18] From the cold mixture free bromine was extracted by a concentrated solution of sodium bromide. Crystallization of the residue from alcohol, using norite, gave long colorless needles of m. p. 208–209°.

Anal. Calcd. for $C_7H_2O_2Br_4$: Br, 73.06. Found: Br, 73.00.

To the mother liquor from the above crystallization water was added, the resulting colorless precipitate extracted with caustic alkali solution, and the extract acidified. Repeated crystallization of the product first from acetic acid and then from a mixture

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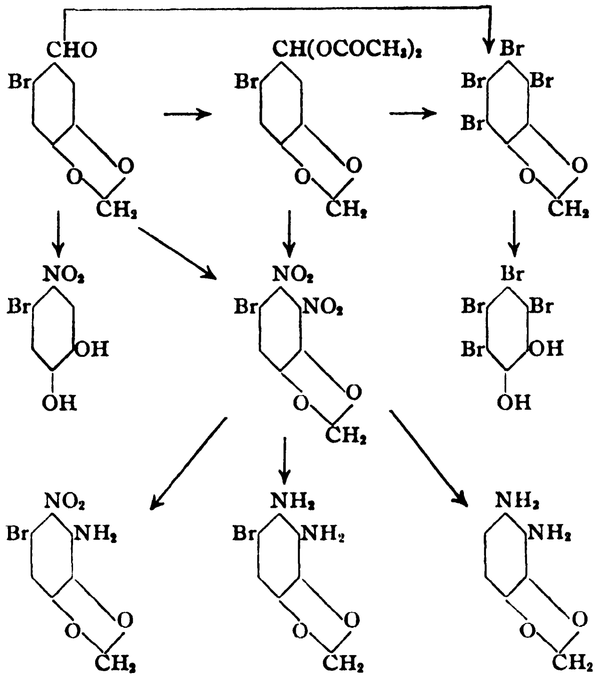
(14) This product is probably identical with that obtained by Herz [*Ber.*, **38**, 2859 (1905)] from methylenedioxynitroanthranilic acid. Here, also, the diamine was not isolated, but its solution was treated with phenanthrenequinone and the condensation product obtained.

(15) Pschorr and Sumuleanu, *ibid.*, **32**, 3410 (1899).

(16) Autenrieth, "Laboratory Manual for the Detection of Poisons and Powerful Drugs" (Warren, tr.), sixth ed., P. Blakiston's Son and Co., Philadelphia, 1928, p. 123.

(17) Parijs, Thesis, Leiden, 1928, p. 150; *Rec. trav. chim.*, **49**, 38 (1930).

(18) When a second portion was heated six hours the ether was split and only the catechol (see below) was isolated. With sodium acetate in the reaction mixture very little splitting occurred.



of benzene and ligroin gave colorless leaflets of tetrabromopyrocatechol; m. p. 190–191°;[19] yield, 37% of purified material.

Anal. Calcd. for $C_6H_2O_2Br_4$: Br, 75.12. Found: Br, 74.90.

The dibenzoyl derivative was obtained in colorless flakes from dilute alcohol; m. p. 197–198°.

Anal. Calcd. for $C_{20}H_{10}O_4Br_4$: Br, 50.47. Found: Br, 50.26.

3-Amino-4-nitro-5-bromocatechol Methylene Ether.—Hydrogen sulfide was bubbled slowly through a mixture of 10 g. of the required dinitro compound,[20] 25 cc. of water and 4 cc. of concentrated ammonia solution at about 60° for several hours while the mixture was shaken[21] continually. The yellow color of the starting material changed to deep reddish-orange. The product was purified repeatedly as follows. To its solution in hot alcohol, a little water was added, the mixture allowed to cool, the gummy deposit removed by filtration and rejected. Further dilution of the filtrate and long standing gave orange crystals. The yield of purified material was about 10%; m. p. 109–110°. When heated above this point the product exploded.

Anal. Calcd. for $C_7H_5O_4N_2Br$: Br, 30.65. Found: Br, 30.81.

A mixture of equal weights of the above-described amine and anhydrous sodium acetate was boiled for thirty minutes with excess of acetic anhydride, and the diacetyl derivative precipitated by adding water to the cold mixture; yield, 60%. Recrystallization from alcohol gave dull yellow plates; m. p. 146–147°. Strong light caused the product to become green and decompose.

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(19) Stenhouse [*Ann.*, 177, 187 (1875)] recorded 187° for this product prepared by action of bromine on protocatechuic acid.

(20) Obtained by the method used by Oelker [*Ber.*, 24, 625 and 2593 (1891)] in preparing his supposed bromodinitropiperonal.

(21) Voorhees with Adams, THIS JOURNAL, 44, 1403 (1922).

Anal. Calcd. for $C_{11}H_9O_6N_2Br$: Br, 23.18. Found: Br, 22.56.

Boiling the diacetyl derivative with a mixture of sodium carbonate and alcohol for an hour converted it into the monoacetyl compound, which separated on addition of water. Crystallization from alcohol gave nearly colorless flakes; m. p. 192–193°.

Anal. Calcd. for $C_9H_7O_5N_2Br$: Br, 26.40. Found: Br, 26.75.

When this product was boiled with acetic anhydride in the presence of sodium acetate it was converted back to the diacetate described above.

3,4-Diamino-5-bromocatechol Methylene Ether.—To a solution of 105 g. of ferrous sulfate in 400 cc. of hot water in a one-liter flask there was added 15 g. of the required dinitro compound, and then 100 cc. of concentrated ammonia water. The mixture was boiled for half an hour, filtered hot, and the filtrate allowed to stand. The crystals that separated were dissolved in hot benzene, boiled with norite, the mixture filtered and three volumes of low boiling ligroin added to the filtrate. A 25% yield of steel-gray plates was obtained; m. p. 89–90° with decomposition.

Anal. Calcd. $C_7H_7O_2N_2Br$: N, 12.12; Br, 34.63. Found: N, 11.96; Br, 34.60.

The dibenzoyldiamino derivative was obtained as colorless needles from alcohol; m. p. 255–256°.

Anal. Calcd. for $C_{21}H_{15}O_4N_2Br$: Br, 18.22. Found: Br, 17.70.

The tetraacetyldiamino derivative was prepared by boiling for fifteen minutes a mixture of equal weights of the amine and anhydrous sodium acetate with excess of acetic anhydride. Water was added to the cold mixture, the resulting liquid concentrated and allowed to crystallize. Recrystallization from dilute acetic acid, after decolorizing with norite, gave colorless flakes; m. p. 133–134°.

Anal. Calcd. for $C_{15}H_{15}O_6N_2Br$: Br, 20.05. Found: Br, 20.43.

3,4-Diaminocatechol Methylene Ether.—A mixture of 10 g. of the dinitrobromo compound, 30 g. of tin and 60 cc. of a 30% solution of concentrated hydrochloric acid in alcohol was heated for an hour under a reflux condenser, cooled, made alkaline with sodium hydroxide, and extracted with ether. Distillation of the ether left a residue that was dissolved in benzene, the solution boiled with norite, filtered, treated with two volumes of low boiling ligroin and allowed to cool. Repetition of this treatment gave 38% of brown solid; m. p. 100–101°.

Anal. Calcd. for $C_7H_8O_2N_2$: N, 18.42. Found: N, 18.43.

3,4-Dihydroxy-6-bromonitrobenzene.—A 50% yield of this product was obtained by treatment of an acetic anhydride solution of 6-bromopiperonal with red fuming nitric acid, sp. gr. 1.6, at 0°. Crystallization from toluene gave yellow needles; m. p. 162–163°.

Anal. Calcd. for $C_6H_4O_4NBr$: Br, 34.18. Found: Br, 34.28.

The diacetyl derivative, obtained in 89% yield, was crystallized in colorless flakes from dilute alcohol; m. p. 117–118°.

Anal. Calcd. for $C_{10}H_8O_6NBr$: Br, 25.15. Found: Br, 25.29.

Summary

Attempts to introduce a second bromine atom into 6-bromopiperonal causes replacement of the aldehyde group by halogen, and the hydrogen bromide formed may open the methylene oxide ring unless sodium acetate is present. Loss of the aldehyde radical could not be prevented by use of the diacetate or the bisulfite addition compound of the starting material. The products isolated were tetrabromocatechol methylene ether and tetrabromocatechol.

It has been shown that reduction of 3,4-dinitro-5-bromocatechol methylene ether may give an aminonitrobromo, a diaminobromo or a diamino compound containing no bromine, depending on conditions of reduction.

Nitration of an acetic anhydride solution of 6-bromopiperonal, as described, replaced the aldehyde radical by the nitro group, split the methylene oxide ring, and gave 3,4-dihydroxy-6-bromonitrobenzene.

Further work is in progress.

IOWA CITY, IOWA

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, VANDERBILT SCHOOL OF MEDICINE]

The Influence of the Migrating Group in the Fries Isomerization

BY R. BALTZLY AND A. BASS

It has hitherto been supposed that the position taken up by the migrating group in the Fries isomerization was determined chiefly, if not entirely, by the structure of the phenol whose ester was used and by the temperature of the reaction mixture. Differences in the metallic halide used as catalyst, and in the solvent, have been considered to affect the speed and completeness of the reaction, but not its direction. That among the esters of normal, fatty acids the nature of the acyl group might be significant has, in fact, been denied by Rosenmund and Schnurr[1] in their work on the course and mechanism of this reaction. In his criticism of Rosenmund's conclusions, v. Auwers[2] did not attack this point. At the same time, Coulthard, Marshall and Pyman[3] have reported formation of *o*-hydroxy ketones of the *m*-cresol series under those conditions in which Rosenmund and Schnurr predicted and *reported formation* of the *para* compounds.

It was of some importance to us to be sure of the nature of the products, so we have carried out isomerizations in this series both at low temperature in nitrobenzene and at high temperature without solvent, and have found that with the esters of the higher fatty acids the same ketone was obtained under both sets of conditions. The products had the properties of *o*-hydroxy ketones and could be methylated and then oxidized to methoxyterephthalic acid.

The *m*-cresyl esters of the lower acids gave varying amounts of *p*-hydroxy ketone. Only in the case of the acetate could Rosenmund's results

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(1) Rosenmund and Schnurr, *Ann.*, **460**, 56 (1926).

(2) v. Auwers and co-workers, *Ber.*, **61**, 416, 1495 (1928); **64**, 2216 (1931); *Ann.*, **460**, 240 (1928); **464**, 293 (1928); **483**, 44 (1930).

(3) Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930). It is to be noted here that these authors employ a system of numbering beginning at the methyl group in the cresol series, whereas we prefer to start with the hydroxyl. Consequently, our 6-butyryl-*m*-cresol is their 4-butyryl compound, and *vice-versa*.

be reproduced. The propionate and butyrate gave merely traces when the reaction was run at room temperature, but when the temperature of the reaction mixture was 2°, the butyrate yielded about 3% of the *p*-hydroxy ketone, while the propionate gave 10% (about 14% of the reacting substance). Lower temperatures of reaction might increase the yield of *p*-hydroxy ketone somewhat, but technical difficulties have prevented our examining this possibility. Lederer,[4] in a study of the behavior of α-naphthyl esters in the Fries isomerization, reports slightly higher yields of *p*-hydroxy ketone with the acetate than with the butyrate, but this may not be significant.

It is probable that the nature of the migrating group exercises a constant effect, larger groups tending to go to the ortho position, but this effect is small compared to that of the structure of the phenol, and the temperature of the reaction. Where these two influences largely counteract each other, the influence of the acyl group may, however, be dominant.

Experimental Part

Fries Isomerizations at High Temperature.—The ester to be isomerized was placed in a flask protected from moisture by a capillary tube, and about 1.1 equivalents of powdered anhydrous aluminum chloride was added as rapidly as the reaction permitted. The flask was placed immediately in an oil-bath and kept at 120–140° until evolution of gas had largely ceased. This usually took 10–20 minutes. The orange-colored mixture was then allowed to cool to around 60° and decomposed with dilute hydrochloric acid. The mixture was extracted with ether, the extract washed with water and dried over calcium chloride. The ether was boiled off and the product fractionated under diminished pressure.

Isomerizations at Low Temperature.—The procedure was essentially the same as that worked out by Rosenmund and Schnurr. The aluminum chloride (1.3 equivalents) was dissolved in a quantity of nitrobenzene five times the weight of ester to be used, and cooled in an ice-bath. The ester was added with vigorous stirring, and the reaction mixture permitted to rise to room temperature. These reactions were allowed to run at least twenty-four hours with stirring. As the higher ketones have only a limited solubility in alkali, it was found more convenient to separate the whole product, after decomposition of the reaction mixture and drying of the extracts, by fractional distillation under diminished pressure.

When the reaction temperature was 2°, the reagents were mixed in a flask cooled by a freezing mixture. The stoppers were coated with paraffin to exclude moisture and the reaction was allowed to run ten days in a refrigerating room, with stirring. In the case of *m*-cresol propionate so treated, 4 g. of *m*-cresol was recovered at the end of the reaction, this corresponding to 17% of the ester used.

The quantities used and the yields of the products are summarized in Table I.

Coulthard, Marshall and Pyman have prepared most of these compounds, and their characterizations agree closely with ours. At the same time, the structure of the higher members depended solely on analogy. It was decided to degrade caproyl *m*-cresol by oxidation. When methylated with sodium methylate and dimethyl sulfate, and then oxidized with hot aqueous

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[4] Lederer, *J. prakt Chem.*, [II] **135**, 49 (1932).

TABLE I

Ester of *m*-cresol used			Temp. of reaction, °C.	*o*-Hydroxy ketone			M. p., phenylhydrazone, °C.	*p*-Hydroxy ketone		
Acyl group	Wt., g.	B. p., °C. (mm.)		Yield		B. p., °C. (mm.)		Yield		M. p., °C.
				G.	%			G.	%	
Propionyl	30	90–92 (5)	120–140	28	93	M. p. 43–44				
Propionyl	21	90–92 (5)	25	15	67	M. p. 43–44		Trace		
Propionyl	36	90–92 (5)	2	23.5	65	M. p. 43–44		3.5	10	117–118
Butyryl	40	89–93 (4)	120–140	30	75	112–115 (4)	97–98			
Butyryl	43	89–93 (4)	25	28	66	112–115 (4)	97–98	Trace		
Butyryl	33	89–93 (4)	2	24	72	112–115 (4)	97–98	1	3	98–99
Valeryl	30	93–95 (2)	120–140	24	80	121–125 (3)	138–139			
Valeryl	20	93–95 (2)	25	14	67	121–125 (3)	138–139			
Caproyl	68	104–105 (2)	120–140	62	91	134–135 (3)	97–97.5			
Caproyl	26	104–105 (2)	25	16	62	134–135 (3)	97–97.5			
Heptylyl	20	112–115 (2)	120–140	14	67	148 (4)	82–83			
Heptylyl	17	112–115 (2)	25	12.5	73	148 (4)	82–83			
Pelargonyl	91	156–162 (4)	120–140	68	75	175–177 (4)				

permanganate solution, it yielded methoxyterephthalic acid, m. p. 278–280°. Consequently, the caproyl group is para to the methyl. The same acid was obtained by similar treatment of 6-acetyl-*m*-cresol.

Summary

In the Fries isomerization the tendency of the fatty acid esters of *m*-cresol to change to *o*-hydroxy ketones, rather than to para, is greater than has hitherto been supposed. This tendency becomes more marked with esters of the higher acids.

NASHVILLE, TENNESSEE

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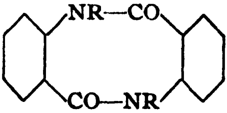
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Anhydrides of N-Arylanthranilic Acids

BY M. GOODMAN, N. ARBITER AND GARFIELD POWELL

Introduction.—Concerning the formulas for the anhydrides of acyl anthranilic acids, of salicylic acids, and of related compounds, there is still some dispute and obscurity.[1] For example, anhydrides of unknown constitution are reported in attempted preparations of chlorides and esters of anthranilic acid,[2] and the only recognized anhydrides of anthranilic acid itself or N-alkyl or N-aryl anthranilic acids are those reported by Schroeter[1b] of the type 2M–$2H_2O$ (M is the original acid) which are formulated as 8-ring compounds . It is the purpose of this communication to show that the hitherto unrecognized acyl anhydride type must be considered in dealing with dehydration products of N-

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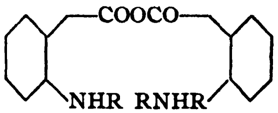
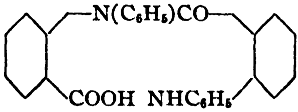
(1) (a) G. Heller and H. Lanth, *Ber.*, **52B**, 2295 (1919); (b) G. Schroeter and O. Eisleb, *Ann.*, **367**, 144 (1909); (c) R. Spallino, *Gazz. chim. ital.*, **37**, II, 151 (1907).

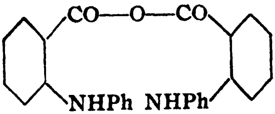
(2) H. Meyer, *Ann.*, **351**, 267 (1907).

aryl anthranilic acids. It seems likely that this type 

is the first product of the reaction of dehydrating agents such as benzene sulfochloride or phosphorus oxychloride on all N-aryl anthranilic acids in pyridine solution.

Theoretical.—When N-phenylanthranilic acid is treated in pyridine solution with benzene sulfochloride, a yellow compound (A) is given in almost theoretical yield. It is insoluble in alkalies or hydrochloric acid hot or cold, but treatment with glacial acetic acid or mild treatment with alcoholic alkalies leads to complete conversion into a white compound (B).

Examination of B points to the formula 2M–H_2O by analysis and determinations of molecular weight. It is soluble in ammonia and a sodium salt can easily be crystallized from water. It is only slowly hydrolyzed by alcoholic potash or hydrochloric acid in glacial acetic acid solution, giving rise to phenylanthranilic acid. On heating it is converted equally into acridone and phenylanthranilic acid, a reaction which, though unpredictable, serves to confirm the formula 2M–H_2O. It can be completely hydrolyzed to N-phenylanthranilic acid but is stable to alcoholic ammonia. The only possible formula seems to be that of N-phenylanthranoylo-N-phenylanthranilic acid .

Examination of (A) also points to the formula 2M–H_2O. On heating it behaves as does (B) and with hydrolytic agents it gives the same results, in all probability through the compound (B) into which it is so easily converted. Its solubilities resemble those of the Schroeter type of anhydride. It is completely converted with alcoholic ammonia into equal parts of phenylanthranilic amide and phenylanthranilic acid. N-Methylanthranilic acid does not give this type of compound in these conditions so the suspicion might arise that the ortho position of the N-aryl substituent is involved. This is not the case, since N-mesitylanthranilic acid gives the same type of anhydride. In the same conditions of preparation, with similar properties, a compound of the type A can also be obtained from N,N-diphenylanthranilic acid, and, as would be expected, it is not convertible into a compound of the B type but is converted immediately by alkalies or glacial acetic acid completely back to the original acid. For the yellow compound, then, the only admissible reaction formula seems to be acyl anhydride .

Since great difficulty has been experienced in attempted syntheses of the esters and chlorides of anthranilic acid and N-substituted anthranilic acids,[2b,3] these anhydrides will be examined for further synthetic uses. Observations already made point to a general production of these A anhydrides and conversion to the peptide compound B in N-arylanthranilic acids. These compounds will be examined in relation to the Schroeter anhydrides.

Experimental

The Yellow Anhydrides (A Compounds)

1. **Phenylanthranilic Anhydride.**—Five grams of N-phenylanthranilic acid was dissolved in 10 cc. of pyridine. Benzene sulfochloride (1.6 cc. = 0.55 mole) was added and the flask shaken and allowed to stand for fifteen minutes. The product was stirred into 200 cc. of cold water and allowed to stand until solid; yield, 5 g., m. p. 145–148°. Repeated crystallization by solution in 15 cc. of chloroform and addition of 30 to 40 cc. of alcohol while hot gave the maximum m. p. of 152–153°, reddening at 149°. A little above the melting point the product lightens in color and appears to solidify (see decomposition by heat). This same product is obtained with *p*-toluene sulfochloride or phosphorus oxychloride, avoiding temperatures above 50° or excess of dehydrating agent. It can also be prepared by reaction in benzene solution with the same dehydrating agents in the presence of anhydrous potassium carbonate.

Anal. Calcd. for $2M-H_2O$: C, 76.43; H, 4.95. For $M-H_2O$: C, 79.9; H, 4.7. Found: C, 77.0, 76.4, 76.6; H, 4.9, 5.1, 4.3. *Mol. wt.* B. p. in benzene = 1.5 M; b. p. in alcohol = 1.8 M.

These analyses and molecular weights are paralleled by others of the same type of compound.

Decomposition by Heat.—Six grams of the anhydride was heated for four minutes at 200° in a test-tube. Melting and partial solidification took place. By collection of the whole product and treatment with dilute ammonia it was separable into 2.6 g. of ammonia-insoluble product and 2.0 g. of ammonia-soluble product (some loss of this portion occurred in recovery from alcohol and clarification through infusorial earth). The ammonia-soluble product had m. p. 179–181°. When crystallized from dilute alcohol it gave no depression of melting point with a specimen of N-phenylanthranilic acid. The ammonia-insoluble product was insoluble in cold concentrated hydrochloric acid, insoluble in alkalies, soluble in alcoholic alkalies, subliming above 310° in the same fashion as a specimen of acridone, giving fluorescent solutions.

Decomposition with Ammonia.—This yellow anhydride, on refluxing with a mixture of alcohol and aqueous ammonia for a few hours, gave evidence of a change to phenylanthranilic acid, some white compound probably of the B type, and a compound of high nitrogen content. When 3 g. of the anhydride in 50 cc. of absolute alcohol, saturated with ammonia, was heated in a bomb tube at 80–90° for two hours, a complete conversion to phenylanthranilic acid and phenylanthranilic amide was observed in the following way. The product was mixed with excess of water and the mixture boiled to remove most of the alcohol and ammonia, sodium hydroxide solution being added so that the concentration was about 4% at the end of the boiling. An insoluble residue, as well as crystals given out on cooling, had m. p. 127.5–128.5, total 1.4 g. These crystals could be recrystallized from a large volume of water or 30% alcohol, m. p. 127.5–128.5. The filtrate, on acidification, gave 1.7 g. of substance of m. p. 174–182°, and, crystallized from dilute alcohol, was shown to be almost wholly phenylanthranilic acid. The neutral product was presumed to be phenylanthranilic amide. To confirm this the amide was

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(3) L. Anschütz and Z. M. Delijski, *Ann.*, **493**, 241 (1932).

prepared as shown below, and had the same m. p. and properties as this neutral compound, giving no depression of melting point on admixture.

The preparation of the methyl ester of phenylanthranilic acid was undertaken. This is described by Schroeter[1b] as unobtainable by the use of hydrochloric acid on a mixture of acid and alcohol. He further states that the reaction of the silver salt of the acid with methyl iodide leads to sticky and uncrystallizable solids. However, the methyl ester had previously been reported[4] as an oil of b. p. 216°, 18.5 mm. Repetition of the silver salt and potassium salt method with methyl iodide led to an oil boiling at 186°, 9 mm. It seemed homogeneous but hydrolysis with alcoholic alkalies led to a recovery of about 80% of phenylanthranilic acid and about 10% of an acid of a distinct bright yellow color. Furthermore, from some specimens of the oil a solid of m. p. 58° slowly crystallized out, undoubtedly one of the pure esters. Accordingly, the preparation was undertaken by the ordinary method with gaseous hydrochloric acid. A good yield of a solid of m. p. 57–58° was obtained. This was the methyl ester, hydrolysis by solution in 5% alcoholic potassium hydroxide and refluxing for fifteen minutes (or until such time as large dilution with hot water gave no precipitate) leading to a total recovery of the original acid.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.98; H, 5.77. Found: C, 73.90; H, 5.81.

It is probable that the Schroeter product contained mixed esters and unchanged acid and that the Baeyer product was the best obtainable from the phenylanthranilic acid used by them, prepared by the method of Graebe.[5]

The methyl ester is colorless, less soluble in ethyl alcohol than the acid itself, and fairly stable to aqueous alkalies. Conversion of this ester into amide was accomplished by heating in absolute ethyl alcohol saturated with ammonia (at 10°) in a bomb tube at 120° for five hours. Even at this temperature the conversion was not complete. The product was poured into water containing potassium hydroxide, most of the alcohol and ammonia boiled off, and the insoluble amide filtered from the cold solution. Crystallized from a large volume of water, the yield was 1 g. of m. p. 127.5–129° from 9 g. of ester. Mixed with the suspected amide from the yellow anhydride, m. p. 127.5–129°.

Anal. Calcd. for $C_{13}H_{12}N_2O$: C, 73.5; H, 5.7; N, 13.2. Found: C, 73.2; H, 6.0; N, 12.91.

Phenylanthranilic amide is colorless, slightly soluble in hot water, soluble in cold concentrated hydrochloric acid.

Decomposition of the Yellow Anhydride with Acids and Alkalies.—The yellow anhydride, by solution in about ten times its weight of 95% acetic acid, and refluxing for a few minutes gives, on dilution with water while refluxing, a white compound of m. p. 200–201°, reddening at 198°, changing just above the melting point, apparently solidifying and lightening in color. The yield is the theoretical (see B).

With aqueous 2% sodium hydroxide the anhydride is apparently not changed on boiling for a few minutes. With alcoholic alkalies, however, a change occurs on solution by heating. The product is again the white compound. By heating with glacial acetic acid containing a small proportion of concentrated hydrochloric acid (1–2%) for fifteen minutes a partial change to phenylanthranilic acid occurs, demonstrated by extraction of this acid either with cold dilute ammonia or 5% sodium hydroxide solution, clarification through infusorial earth, and crystallization from dilute alcohol.

Drastic treatment with alcoholic alkalies leads to a further decomposition of the white compound into a total yield of phenylanthranilic acid. Thus 1.4 g. of the white compound (B) was refluxed for eight hours with 15 g. of potassium hydroxide in 100 cc. of 80% alcohol. On dilution with 700 cc. of water, filtration, precipitation with acetic

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(4) A. Baeyer and V. Villiger, *Ber.*, **37**, 3201 (1904).

(5) Graebe and Lagodinski, *Ann.*, **276**, 43 (1893).

acid, 1.4 g. of an acid was obtained. This acid gave no residue when taken up in 200 cc. of 7% sodium hydroxide (the B compound would come out as sodium salt) and, on recovery by acidification, an acid of m. p. 178–182° was obtained. Dissolved in alcohol, the solution clarified, and crystallized by addition of a large excess of water, the acid came out of m. p. 183–184°, yield 1.3 g., giving no depression with phenylanthranilic acid of m. p. 183–184°. Treatment of the anhydride with methyl alcohol at 100° for seven hours leads to the white compound (B) and not to esters.

2. **N,N-Diphenylanthranilic Anhydride.**—This anhydride is not so readily formed as the previous anhydride. Since high temperatures must be avoided to prevent acridone formation, or other products, it is best to accept a small yield. Seven grams of N,N-diphenylanthranilic acid was dissolved in 30 cc. of pyridine and benzene sulfochloride (1 mole = 3.5 cc.) was added. The mixture was warmed to 50° and allowed to stand at that temperature for five minutes. When the reaction mixture was poured into water the product came out as a sticky mass. The water was decanted and the mass washed with water by decantation a few times. The mass was then pressed under alcohol, the alcohol decanted, and finally taken up in a little chloroform, thrown out with warm 95% alcohol; yield 4.5 g., m. p. 143–145°. Recrystallization in the same way gave a maximum m. p. of 144.5–146° (uncorr.).

Anal. Calcd. for $2M-H_2O$: C, 81.40; H, 5.03. Found: C, 81.60, 81.24; H, 5.00, 5.20.

On heating above the melting point this anhydride also suffered a change, not investigated. It was easily hydrolyzed; 2.4 g. refluxed with 80% acetic acid for five minutes (keeping in solution by further addition of glacial acetic acid if necessary) gave a crude yield of an acid, 2.3 g., m. p. 199–202°. When this acid was taken up in cold dilute ammonia, clarified by filtration through infusorial earth, and reprecipitated, it was obtained in yield of 2.2 g., m. p. 202–203°. Mixed with N,N-diphenylanthranilic acid of m. p. 202–203°, it gave no depression of the melting point. The same result is obtained if heated for a few minutes in solution in alcoholic potassium hydroxide. That is, with gentle hydrolytic treatment there was observed no formation of a compound of the B type. In the preparation of this anhydride there are probably present some traces of N-phenylacridone, evident after hydrolytic treatment as a trace causing turbidity in the ammoniacal solution. If higher temperature was used in the preparation, sufficient of this impurity could be recovered after hydrolysis to give an m. p. of 273–275° and characteristics of N-phenylacridone which has an m. p. of 276°.

The Peptide Compounds (B)

3. **N-Phenylanthranoylo-N-phenylanthranilic Acid.**—This is prepared from the yellow anhydride, as stated, by mere solution in hot acetic acid. It can also be prepared by gentle treatment with alcoholic potash but is best crystallized from acetic acid solution, hot, by the gradual addition of hot water. Crystallization from dilute alcohol is liable to lead to a low melting (probably hydrated) form of greater solubility and so only succeeds when slowly done. Thus, if a specimen of this acid is taken up in dilute sodium hydroxide solution, precipitated with acetic acid and collected and washed, it appears on the filter paper with a slight yellow tinge. When pressed apparently dry it gives off water near 120° without melting. Also, in this form, it goes readily into solution in alcohol or benzene, but, on continued heating, comes out again absolutely colorless. It is, indeed, only slightly soluble in benzene, alcohol or chloroform, coming out of solution slowly in very small crystals, m. p. as given. Above its melting point it lightens in color, apparently solidifying, exactly as does the yellow anhydride at its lower melting point; 2 g. of this acid was held at 220° in a test-tube for three minutes. The product was crushed under dilute ammonia, giving 0.90 g. of ammonia-soluble product of m. p. 176–180° which, on crystallization from dilute alcohol, is identified as N-phenylanthra-

nilic acid. The residue of 0.95 g. was acridone. When treated with alcoholic ammonia in a bomb tube, it is unchanged at 120° for five hours (unlike the 8-ring anhydride of Schroeter). As has been previously stated, it can be completely hydrolyzed to phenylanthranilic acid.

Anal. Calcd. for $2M-H_2O$: C, 76.43; H, 4.95. Found: C, 76.85; H, 5.17. *Mol. wt.* B. p. in chloroform = 1.0 M; f. p. in acetic acid = 1.1 M; f. p. in camphor = 1.5 M.

The nearest analog of this compound is anthranoylo-N-phenylanthranilic acid described by Schroeter[1b] and prepared by the reduction of the nitro compound. In encountering the yellow anhydrides it was naturally suspected that they would correspond to the $2M-2H_2O$ compounds of Schroeter and that the white acids were formed by hydrolysis. The molecular weight determinations are curious, lower than expected and much lower than the consistently normal results by Schroeter. A possibility of unknown N-arylanthranils could not be overlooked, nor molecular combinations of previously described dehydration products of the anthranilic acids. The complexities are illustrated by a test preparation in isoquinoline, leading to a compound analyzing $2M-H_2O$ + isoquinoline, from which the isoquinoline could be recovered. One might well expect, therefore, analyses $3M-H_2O$ for other members of this series. The carbon figure is the only significant variant (by about 1%) for the different possibilities. The results given here are supported by other results with N-arylanthranilic acids to be given later.

Summary

1. An argument for the acyl anhydride formula for certain dehydration products of N-arylanthranilic acids.

2. The transformations of N-phenylanthranilic anhydride by heat to acridone, by ammonia to N-phenylanthranilic amide, by solution in certain media to (probably) N-phenylanthranoylo-N-phenylanthranilic acid.

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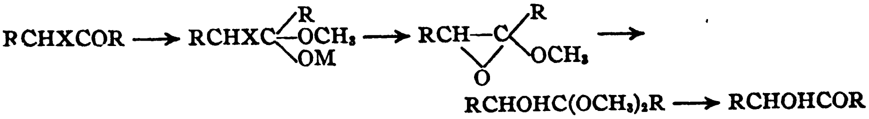
The Reactions of Halogenated Ketones.
II. The Action of Potassium Cyanide on Desyl Chloride

BY E. P. KOHLER AND F. W. BROWN

Recent investigations have indicated that the formation of alpha hydroxy ketones from the corresponding halogen compounds occurs in a series of steps which may be represented as follows[1]



In view of these and similar results it seems not improbable that the carbonyl group participates in most of the reactions of alpha halogenated

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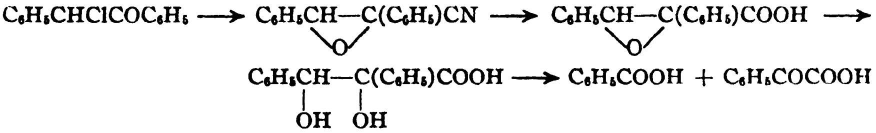
(1) Ward, *J. Chem. Soc.*, 1541 (1929); Kohler and Addinall, THIS JOURNAL, 52, 3728 (1930); Bergmann and Miekeley, *Ber.*, 64, 802 (1931).

ketones and that the direct replacement of the halogen atom occurs rarely if ever. In order to secure more information on the subject and in particular to isolate the hypothetical intermediate oxides we have studied the reaction between potassium cyanide and desyl chloride. If this reaction involved direct replacement of the halogen it would result in the formation of an alpha cyano ketone which is known, and if it began with the addition to carbonyl it would be expected to lead to an oxide which would be sufficiently stable for isolation. The reaction gives rise to a considerable number of products but neither the cyano ketone nor any substance derived from it could be found. In this case, therefore, there is no direct replacement of the halogen.

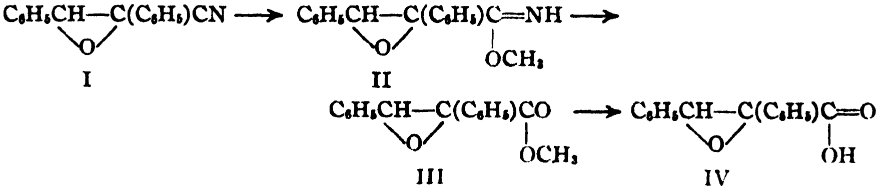
Among the products of the reaction between the cyanide and the halogenated ketone are two substances which have the composition of the cyano ketone but which have quite different properties. By suitable manipulations these substances can be converted into the corresponding acids. These acids combine with water to form dihydroxy acids and each of them can be oxidized to equivalent quantities of benzoic and phenylglyoxylic acids. The dihydroxy acids must come from oxido acids and the oxidation products show that the phenyl groups are in their original positions. In this case, therefore, the reaction involves the carbonyl group and the proof of intermediate oxides is explicit.



$$C_6H_5CHClCOC_6H_5 \longrightarrow C_6H_5\underbrace{CH-C}_{O}(C_6H_5)CN \longrightarrow C_6H_5\underbrace{CH-C}_{O}(C_6H_5)COOH \longrightarrow$$

$$C_6H_5\underset{OH}{CH}-\underset{OH}{C}(C_6H_5)COOH \longrightarrow C_6H_5COOH + C_6H_5COCOOH$$

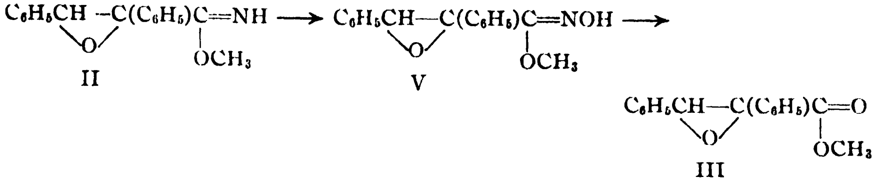
The stereoisomeric oxido nitriles which are formed in this manner are comparatively stable substances. They do not readily undergo the usual rearrangement of oxides to ketones, presumably because they contain no active hydrogen, and they also show no tendency to polymerize. Their behavior is that of uncommonly active nitriles. In feebly alkaline solutions, for example, they combine with alcohols, and since addition to the cyanogen group is much more rapid than to the oxide ring, they are thus converted into imino ethers in which the ring is intact. Like other imino ethers these substances are readily hydrolyzed to esters, and the esters in turn can be hydrolyzed to the corresponding oxido acids



$$\underset{\text{I}}{C_6H_5\underbrace{CH-C}_{O}(C_6H_5)CN} \longrightarrow \underset{\text{II}}{C_6H_5\underbrace{CH-C}_{O}(C_6H_5)\underset{OCH_3}{C}{=}NH} \longrightarrow$$

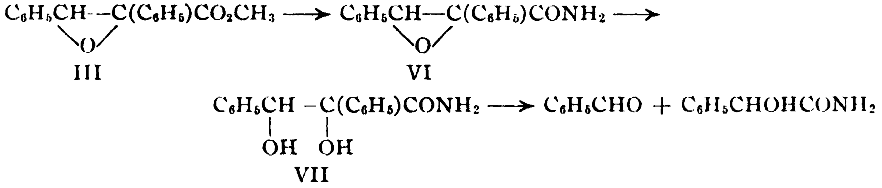
$$\underset{\text{III}}{C_6H_5\underbrace{CH-C}_{O}(C_6H_5)\underset{OCH_3}{CO}} \longrightarrow \underset{\text{IV}}{C_6H_5\underbrace{CH-C}_{O}(C_6H_5)\underset{OH}{C}{=}O}$$

Like some other imino ethers, also, these substances can be converted into hydroxyimino ethers which likewise are hydrolyzed to the corresponding esters, but which cannot be regenerated from the esters



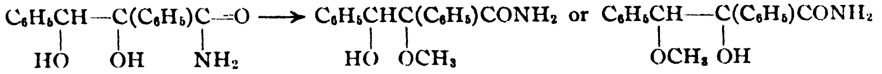
II V III

In all the foregoing transformations in which the ring is left intact the isomers behave alike and the stereoisomerism is maintained, each isomer giving rise to a single product. Under more vigorous treatment the ring is opened but here the isomers, as would be expected, react with unequal ease and, since the reactions involve the asymmetric carbon atoms, the isomerism at times becomes confused. Thus concentrated aqueous ammonia converts the higher melting ester into the amide of a dihydroxy acid, although its action on the lower melting isomer stops with the formation of the oxido amide. And when either the oxido amide or the dihydroxy amide is digested with dilute sulfuric acid it is transformed into an isomeric dihydroxy amide. In this case, therefore, the final product from both esters is the same



III VI VII

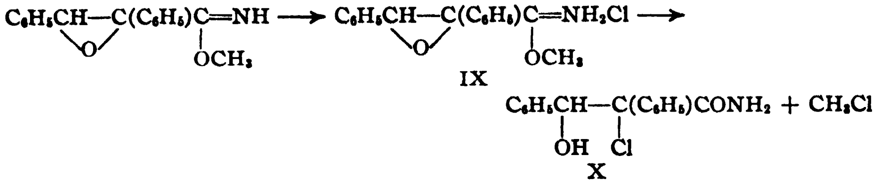
Methyl alcoholic acid converts each of the isomeric dihydroxy amides into the same mixture of mono methylated amides. Although it is not clear whether these isomeric methylation products are structural or spatial isomers, it is evident that both amides cannot form the same mixture without the isomerization of at least one of them



$$\underset{\mathrm{HO}}{\mathrm{C_6H_5CH}}-\underset{\mathrm{OH}}{\mathrm{C}}(\mathrm{C_6H_5})\underset{\mathrm{NH_2}}{\mathrm{C}}{=}\mathrm{O} \longrightarrow \underset{\mathrm{HO}}{\mathrm{C_6H_5CH}}\underset{\mathrm{OCH_3}}{\mathrm{C}}(\mathrm{C_6H_5})\mathrm{CONH_2} \text{ or } \underset{\mathrm{OCH_3}}{\mathrm{C_6H_5CH}}-\underset{\mathrm{OH}}{\mathrm{C}}(\mathrm{C_6H_5})\mathrm{CONH_2}$$

VIII

Possibly a similar difference in the ease with which the ring is opened in the case of the isomeric imino ethers is responsible for the difference in the behavior of these substances toward hydrogen chloride but it seems more probable that here relative solubilities play a major role. In ether the higher melting imino ether rapidly forms a sparingly soluble hydrochloride which very slowly loses methyl chloride, redissolves, and forms a chloro hydroxy amide. Under the same conditions the isomeric imino ether is rapidly transformed into an isomeric chlorohydroxy amide.



$$C_6H_5CH\overset{O}{—}C(C_6H_5)\underset{OCH_3}{C}{=}NH \longrightarrow C_6H_5CH\overset{O}{—}C(C_6H_5)\underset{OCH_3}{C}{=}NH_2Cl \longrightarrow$$

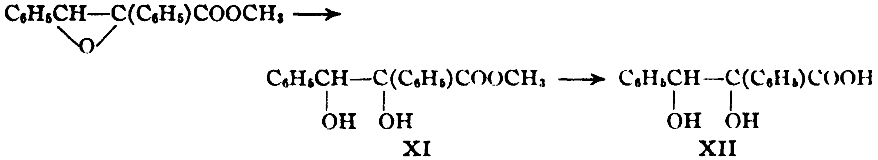
IX

$$\underset{OH}{C_6H_5CH}—\underset{Cl}{C}(C_6H_5)CONH_2 + CH_3Cl$$

X

We have not succeeded in determining whether the isomerism of these chlorohydrins is structural or spatial. They are both very reactive; even a very dilute base rapidly changes the one (180°) into a dihydroxy amide (135°), and the other into the oxido amide (124°) which could not be obtained from the corresponding ester.

Naturally, the oxido compounds are most easily changed into the corresponding open chained esters and acids. This can be accomplished both with acids and bases; but when the oxido esters are turned into dihydroxy esters with acids, there is probably no change in configuration because each ester gives a single product, while treatment of the esters or acids with bases may lead to a mixture of dihydroxy acids:



$$C_6H_5CH\overset{O}{—}C(C_6H_5)COOCH_3 \longrightarrow$$

$$\underset{OH}{C_6H_5CH}—\underset{OH}{C}(C_6H_5)COOCH_3 \longrightarrow \underset{OH}{C_6H_5CH}—\underset{OH}{C}(C_6H_5)COOH$$

XI XII

As will be seen from the foregoing account, these oxido compounds, which belong to a type that it would be difficult to secure in any other manner, differ from other oxido compounds which contain an additional functional group mainly in two respects; they do not undergo rearrangement to isomeric oxido compounds and they show no tendency to polymerize.

Experimental Part

In order to secure adequate concentrations of both reactants it is necessary to carry out the reaction between potassium cyanide and desyl chloride in aqueous alcoholic solutions. Since these solutions contain appreciable quantities of hydroxide and alcoholate, some of the desyl chloride is inevitably transformed into by-products. These were isolated in part but they need not be considered here because they have been described in the meanwhile by Madelung and Oberwegner.[2] In addition to these by-products there are also secondary products which are due to the reaction between the oxido nitriles and alcohol in the slightly alkaline medium—mainly the imino ethers. Since these imino ethers are formed under all conditions, are useful intermediates in the conversion of the nitriles into other substances and are the only organic compounds which can be separated from the reacting mixture without distillation, we generally found it expedient to allow the reaction to run until most of the oxido nitriles had disappeared. Our procedure thus became as follows.

A mixture obtained by pouring together a solution of one mole of desyl chloride in three times its weight of alcohol and a solution of 1.5 moles of potassium cyanide in a

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(2) Madelung and Oberwegner, *Ann.*, **490**, 201 (1931).

minimum quantity of water, was left to itself at the ordinary temperature for four days. It was then diluted with several times its volume of water and extracted with ether. The extract, when dried and evaporated, left a solid suspended in a red or brown oil.

The solid was recrystallized from benzene-petroleum ether and thus eventually separated into the two imino ethers melting at 110 and 85°. The oily liquid was fractionated under diminished pressure. The lowest boiling fraction (100–110°, 4 mm.) was composed largely of methyl benzoate; the second fraction (150–155°) yielded the lower melting oxido nitrile which after recrystallization from petroleum ether melted at 52°; the third fraction (160–165°) contained the isomeric oxido nitrile which after purification melted at 72°, and the highest fraction was composed largely of benzamide and desoxybenzoin. The yield of the principal product—the imino ether melting at 110°—was about 30% and the total yield of nitriles and imino ethers about 50%.

The relation between the nitriles and the imino ethers was established by converting the one into the other. This conversion was readily accomplished by dissolving a small quantity of the nitrile in dry methyl alcohol, adding an equal weight of dry potassium cyanide and setting the mixture aside for several days. The yield was almost quantitative and each nitrile gave a single imino ether, the lower melting ether being formed from the lower melting nitrile. The corresponding hydroxy imino ethers were obtained with equal ease by first converting the nitriles into imino ethers and then digesting the ethers with methyl alcoholic hydroxylamine.

As was to be expected, both imino ethers were very rapidly hydrolyzed to the corresponding oxido esters. We employed for the purpose dilute solutions of sulfuric acid in dry methyl alcohol and obtained almost quantitative yields. Here also each isomer gave a single product and the lower melting methyl ester was formed from the lower melting ether.

The oxido esters were hydrolyzed to the corresponding oxido acids without difficulty by warming them gently with a slight excess of dilute methyl alcoholic potassium hydroxide. The yields were excellent and each ester gave a single acid, the lower melting acid corresponding to the lower melting ester.

The corresponding pair of isomeric oxido amides was not obtained quite so easily. For while concentrated aqueous ammonia turns the lower melting oxido ester into the amide it converts the higher melting isomer into an open-chained compound. In order to obtain the isomeric amide it was necessary first to transform the higher melting ester into an open chained compound by passing hydrogen chloride through its solution in ether or benzene until the precipitated hydrochloride redissolved, and then to reclose the ring by treating the resulting chlorohydrin with dilute sodium carbonate.

None of the foregoing oxido compounds reduced permanganate but the oxido esters and the oxido acids rapidly reduced the usual solutions of chromic oxide in glacial acetic acid. The esters were thus oxidized to phenylglyoxylic ester and a mixture of benzoic and phenylglyoxylic acids and the acids were oxidized to equivalent quantities of benzoic and phenylglyoxylic acids.

The analytical results and the melting points of the oxido compounds are shown in the following table in which the substances which have the same configuration are grouped together.

The manner in which the various oxido compounds were transformed into the corresponding open-chained derivatives has been outlined in the introduction. In general the oxide ring can be opened equally well by digesting the substance with a strong acid or a strong base and the choice of the agent depends on the character of the functional group. Since the isolation of the open-chained compound presents no complications it is unnecessary to describe the experiments in detail. The melting points and the composition of the various compounds, and the oxido compounds from which they were obtained (sources), are shown in the following table.

TABLE I

Formulas Empirical	Structural	M. p., °C.	Calculated M	Calculated C	Calculated H	Calculated N	Calculated OCH$_3$	Found M	Found C	Found H	Found N	Found OCH$_3$
$C_{15}H_{11}ON$	I	52	221	81.4	5.0			220	81.4	5.2		
$C_{16}H_{15}O_2N$	II	85	253	75.9	6.0	5.5	12.3	243	75.9	6.0	5.7	12.1
$C_{16}H_{14}O_3$	III	35	254	75.6	5.5		12.2	240	75.5	5.6		12.1
$C_{15}H_{12}O_3$	IV	90	240	75.0	4.8				75.1	4.9		
$C_{16}H_{15}O_3N$	V	150		71.4	5.6				71.3	5.5		
$C_{15}H_{13}O_2N$	VI	205		75.3	5.4	5.9			75.2	6.0	6.1	
$C_{15}H_{11}ON$	I	74	221	81.4	5.0			222	81.2	5.2		
$C_{16}H_{15}O_2N$	II	110	253	75.9	6.0	5.5	12.3	241	75.8	5.9	5.7	12.0
$C_{16}H_{14}O_3$	III	80	254	75.6	5.5		12.2	240	75.5	5.5		
$C_{15}H_{12}O_3$	IV	121	240	75.0	4.8			241	74.8	5.4		
$C_{16}H_{15}O_3N$	V	172	240	71.4	5.6		11.52		71.4	5.4		11.3
$C_{15}H_{13}O_2N$	VI	124		75.3	5.4				75.3	5.8		

TABLE II

Formulas Empirical	Structural	M. p., °C.	Calculated M	Calculated C	Calculated H	Calculated N	Calculated OCH$_3$	Found M	Found C	Found H	Found N	Found OCH$_3$	Source
$C_{15}H_{15}O_3N$	VII	135		70.0	5.9	5.5			69.9	5.7	5 6		II
$C_{15}H_{15}O_3N$	VII	235		70.0	5.9				69.8	6.1			
$C_{16}H_{17}O_3N$	VIII	178		70.8	6.2		11.4		70.8	6.1		11.3	VI, VII
$C_{16}H_{17}O_3N$	VIII	250		70.8	6.2		11.4		70.9	6.1		11.4	VI, VII
$C_{15}H_{14}O_2NCl$	X	180		65.4	5.1				65.4	5.0			II (85°)
$C_{15}H_{14}O_2NCl$	X	210	276	65.4	5.1	12.9	11.4	280	65.5	5.0	12.4		II (110°)
$C_{16}H_{16}O_4$	XI	144		70.6	5.9		11 3		70.4	5.8	11.1		III (35°)
$C_{16}H_{16}O_4$	XI	153		70.6	5.9				70.5	5.8			III (80°)
$C_{15}H_{14}O_4$	XII	184		69.8	5.4				69.6	5.5			III, XI
$C_{15}H_{14}O_4$	XII	204		69.8	5.4				69.2	5.8			III, XI

Summary

The action of potassium cyanide on desyl chloride involves the carbonyl group and results in the formation of two stereoisomeric oxido nitriles. No substances formed by direct replacement of chlorine could be detected among the products of the reaction.

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The Constitution of Pyromellitic, Mellophanic and Prehnitic Acids

BY LEE IRVIN SMITH AND GORDON D. BYRKIT

No proof of the constitution of the three isomeric benzene tetracarboxylic acids has apparently been offered in which they have been converted into compounds of known orientation. Numerous syntheses have made it certain that pyromellitic acid is the 1,2,4,5-tetracarboxylic acid. Such procedures in the case of the 1,2,3,4- and the 1,2,3,5-acids, however, have led to conflicting results.[1] The purpose of the investigation presented in this paper has been to make the orientation of these other two acids certain by converting one of them to a compound of known orientation. The importance of such a structure proof is apparent from the wide use of these acids as reference compounds.

Baeyer[2] separated "isopyromellitic acid" into these two isomeric acids, naming one of them prehnitic acid, and determining the orientation of this acid as 1,2,3,5.

Jacobsen[3] oxidized the hydrocarbon resulting from the action of sodium and methyl iodide on bromomesitylene, and obtained a tetrabasic acid having the properties of Baeyer's mellophanic acid. Tohl[4] prepared prehnitene from pentamethylbenzene by means of the Jacobsen reaction, and on oxidizing this hydrocarbon, obtained an acid having the properties of Baeyer's prehnitic acid.

In 1910, Carré[5] treated mesitylmagnesium bromide with paraformaldehyde, and the resulting carbinol, on oxidation, gave an acid agreeing in properties with Baeyer's mellophanic acid. Bamford and Simonson,[6] using almost the same series of reactions, prepared a tetrabasic acid softening at 240° and melting at 252°, which gave a tetramethyl ester melting at 108–109°. These are the properties of Baeyer's prehnitic acid. In addition, Bamford and Simonson, by oxidizing 1,4-dimethylnaphthalene, succeeded, after much difficulty, in isolating from the reaction mixture an acid sintering at 225° and melting at 238°, which gave a tetramethyl ester melting at 133–135°; these are the properties of Baeyer's mellophanic acid.

Hence from the work of Jacobsen, Tohl and Carré, it appears that Baeyer had assigned incorrect orientations to these two acids, and that mellophanic acid should be 1,2,3,5 and prehnitic acid 1,2,3,4; while from the work of Bamford and Simonson, the orientation as Baeyer originally assigned it is correct and prehnitic acid is the 1,2,3,5, while mellophanic acid is the 1,2,3,4.

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[1] The 1,2,3,4-acid has usually been called mellophanic (but sometimes prehnitic acid) and assigned the melting point 238° (225–241°). Conversely, the 1,2,3,5-acid has usually been called prehnitic (sometimes mellophanic) and assigned melting points varying between 237 and 262° (usually about 250°).

[2] Baeyer, *Ber.*, **2**, 94 (1869); **4**, 273 (1871); *Ann. Suppl.*, **7**, 20 (1870); *Ann.*, **166**, 325, 628 (1873).

[3] Jacobsen, *Ber.*, **17**, 2517 (1884).

[4] Tohl, *ibid.*, **21**, 904 (1888).

[5] Carré, *Compt. rend.*, **151**, 151 (1910).

[6] Bamford and Simonson, *J. Chem. Soc.*, **97**, 1904 (1910).

The results of our investigation are in agreement with those of Bamford and Simonson. Mesitylene carboxylic acid, prepared both by their method and by the haloform reaction, gave identical products agreeing in properties with their acid. Part of this sample was oxidized to the 1,2,3,5-acid, which was the same as theirs. Part of it was nitrated, the oxidation completed and the dinitrotetracarboxylic acid decarboxylated. Since the resulting product was *m*-dinitrobenzene, the carboxyl groups certainly occupied the 1-, 2-, 3- and 5-positions. This makes it certain that the acid melting at 237–250°, Baeyer's prehnitic acid (tetramethyl ester melting at 108–109°), is the 1,2,3,5-acid. Since, in addition to this, it is possible to decarboxylate diaminopyromellitic acid to *p*-phenylenediamine, the third acid melting at 238° (240°) Baeyer's mellophanic acid (tetramethyl ester melting at 133–135°) must be the 1,2,3,4-acid.

We consider the constitution of these acids now made certain by this agreement with and extension of the work of Bamford and Simonson. It is difficult to explain the result of Jacobsen, Tohl and Carré, but the suggestion of Bamford and Simonson that prehnitene is 1,2,3,5-tetramethylbenzene cannot be accepted, since all the many syntheses of isodurene, as well as its reactions, indicate that isodurene is the 1,2,3,5-tetramethylbenzene. With regard to the nomenclature, however, we propose the following change: Since the constitution of prehnitene is known to be 1,2,3,4-tetramethylbenzene, it is essential to clarity that benzene-1,2,3,4-tetracarboxylic acid be known as prehnitic acid. Likewise mellophanic acid must be the term applied to benzene-1,2,3,5-tetracarboxylic acid.

Experimental Part

I. Pyromellitic Acid Series

Acetylpseudocumene.—The method of Maxwell and Adams[7] was used; b. p. 114–116° (7 mm.).

Durylic Acid.—The haloform reaction described by Mills[8] and investigated by Fuson[9] was used with the following modifications. The reaction mixture was refluxed for five hours and excess bromine discharged by sodium bisulfite. The unchanged acetylpseudocumene as well as bromoform and carbon tetrabromide were extracted with ether. The purification of the sodium salt gave very satisfactory results provided the gelatinous material not dissolved by alkali was carefully filtered off. Crystallization of the sodium salt from acetone was omitted but the acid obtained melted at the same temperature given by Mills (148–149°).

Pyromellitic Acid.—The acid obtained by the method of Mills[8] by the oxidation of durylic acid sintered at 235°, melted at 270–272°.

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(7) Maxwell and Adams, This Journal, 52, 2969 (1930).

(8) Mills, *J. Chem. Soc.*, 101, 2191 (1912).

(9) Fuson, *et al*, This Journal, 52, 3269 (1930); 53, 1985, 3494, 4097 (1931).

Dinitrodurylic Acid.—This was obtained from durylic acid by the method of Nef.[10] An acid melting at 212.5–214.5° (corr.) was obtained through the following purification. The crude acid was suspended in a small amount of water and dilute sodium hydroxide added to faint alkalinity. The solution was warmed and the undissolved material (trinitropseudocumene) filtered off. The filtrate was acidified, the acid filtered off and washed with water. It was dissolved in the minimum amount of 95% alcohol, *slightly* warmed. Sufficient water was added to begin precipitation and then alcohol to redissolve. After standing *uncovered* overnight, the crystals were filtered off, allowed to effloresce in air for two hours and then dried in the oven at 60°.[11]

Dinitropyromellitic Ester.—The oxidation of dinitrodurylic acid and esterification of the dinitropyromellitic acid was done according to Nef[10] except that the latter acid need not be isolated. To a hot solution of 10 g. of the purified calcium salt of dinitropyromellitic acid in 200 cc. of water was added hot ammonium oxalate solution containing a little ammonia until precipitation was just complete. The calcium oxalate was filtered off and to the hot filtrate was added a hot solution of silver nitrate as long as precipitation occurred. The silver salt was filtered off and dried at 100°; yield 18 g. or 97.8%.

This silver salt was converted to the ester as described by Nef[10] by refluxing with ethyl bromide in dry ether, yellow crystals of m. p. 127–128°.

Diaminopyromellitic Ester.—Nef's directions[10] for the reduction of dinitropyromellitic ester with zinc and acetic acid were used. On pouring the reaction mixture into water, a yellow solid was precipitated which changed quickly to a brilliant scarlet; m. p. 133–134°.

Decarboxylation.—0.4 g. of potassium hydroxide and 1.0 g. of diaminopyromellitic ester were dissolved in 25 cc. of 95% alcohol and refluxed four hours. The solution was evaporated to dryness, mixed with an equal weight of soda lime and dry distilled; 0.25 g. (93%) of a yellow solid distilled over; m. p. 136–137°. Mixed with *p*-phenylenediamine (m. p. 136–137°), there was no depression of the melting point.

The diacetyl derivative of the yellow solid was prepared according to the directions of Mulliken[12] with acetic anhydride. The product melted at 302–303° and mixed with known diacetyl-*p*-phenylenediamine (m. p. 303–304°), showed no depression of the melting point.

II. The 1,2,3,5-Series

Mesitylene Carboxylic Acid.—Mesitylmagnesium bromide was carbonated by passing a stream of pure, dry, carbon dioxide through the ethereal solution overnight. The reaction mixture was worked up in the usual way. The crude acid was recrystallized from the minimum amount of carbon tetrachloride; yield 37 g. (53.7%) taking into account the recovery of 16 g. of bromomesitylene; m. p. 151–152°.

Acetylmesitylene.—This was prepared by the method of Meyer and Molz.[13]

Mesitylene Carboxylic Acid from Acetylmesitylene.—In the case of acetylmesitylene, hypobromite gave an ω,ω,ω-tribromoacetylmesitylene which was not hydrolyzed by the alkali used.[9] Houben and Fischer[14] obtained a quantitative yield on hydrolyzing ω,ω,ω-trichloroacetylmesitylene by boiling two hours with 40% alkali. By this method, however, the tribromo compound gave rise to considerable tar and only 16% yield of the acid. The product melted at 145–147° and mixed with mesitylene carboxylic acid prepared by the Grignard method it melted at 148.5–150°.

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(10) Nef, *Ann.*, **237**, 1 (1887).

(11) Gissmann, *ibid.*, **216**, 200 (1883).

(12) Mulliken, "Identification of Pure Organic Compounds," Vol. II, p. 112.

(13) Meyer and Molz, *Ber.*, **30**, 1271 (1897).

(14) Houben and Fischer, *ibid.*, **63B**, 2458 (1930).

Benzene-1,2,3,5-tetracarboxylic Acid.—This was prepared in precisely the same way as pyromellitic acid, oxidizing mesitylene carboxylic acid instead of durylic acid; m. p. 238–253°.

Benzene-1,2,3,5-tetramethyl Carboxylic Ester.—One gram of the acid was suspended in 100 cc. of ether and treated with the diazomethane from 3 cc. of nitroso methylurethan. The yellow color slowly faded, but not much gas was evolved. Two more similar portions of diazomethane were added, the solution then filtered and the filtrate evaporated. The residue was crystallized twice from methyl alcohol; m. p. 107–109°.

Dinitromesitylene Carboxylic Acid.—This was prepared according to Nef's[10] directions for dinitrodurylic acid and purified as described above for dinitrodurylic acid. The yield was 27 g. (87.1%) from 20 g. of mesitylene carboxylic acid; m. p. 231–232°.

Dinitrobenzene-1,2,3,5-tetracarboxylic Acid.—Four grams of dinitromesitylene carboxylic acid was dissolved in a solution of 10 g. of potassium carbonate in 400 cc. of water, 14.5 g. of potassium permanganate was added, and the mixture heated on the steam-bath until the color faded (four days). Then 0.5 g. of potassium permanganate was added and the heating continued two more days. The slight color was discharged by sodium bisulfite and the manganese dioxide filtered off and washed. The filtrates were combined, concentrated and acidified, then extracted several times with ether and the ether evaporated. The residue was dissolved in water and treated with excess barium carbonate and filtered. Alcohol was added to the cold filtrate slowly with stirring until, on standing an hour, additional alcohol caused no further precipitation.[15] The barium salt was filtered off, dissolved in water and excess of 50% sulfuric acid added. Without filtering, the mixture was extracted several times with ether. The extracts were evaporated to dryness on the steam-bath and finally dried in a vacuum desiccator over concentrated sulfuric acid for several days; yield, 1 g. (12%); m. p. 216–218°. The acid contains three molecules of water of crystallization.

Anal. Calcd. for $C_{10}H_4O_{12}N_2 \cdot 3H_2O$: C, 30.15; H, 2.51. Found: C, 29.9; H, 2.59. Loss of H_2O at 110°, found, 2.97, 3.04 moles. *Anal.* of anhydrous acid, $C_{10}H_4O_{12}N_2$: Calcd. C, 34.88; H, 1.16. Found: C, 35.1; H, 1.16.

Decarboxylation of Dinitrobenzene-1,2,3,5-tetracarboxylic Acid.—2.0 grams of the acid, 4 g. of quinoline and 0.4 g. of copper chromite[16] were heated at 160° for four hours, then at 210° for two hours.[17] The mixture was taken up in 10 cc. of ether, washed with dilute hydrochloric acid and water. The ether on evaporation left 0.65 g. (65%) *m*-dinitrobenzene; m. p. 79–82°. This was recrystallized from alcohol; yield 0.5 g.; m. p. 85.5–86.5°. Mixed with known *m*-dinitrobenzene (m. p. 85–86°) it melted at 85–86°.

Summary

By relating two of them to compounds of known orientation, it has been shown that of the three isomeric benzene tetracarboxylic acids, the one melting at 270–272° is the 1,2,4,5-acid, the one melting at 238–253° is the 1,2,3,5-acid while the one melting at 238° (240°) by elimination must be the 1,2,3,4-acid. It is suggested that these compounds should be called pyromellitic, mellophanic and prehnitic acids, respectively.

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[15] The calcium salt of this acid is precipitated from water by alcohol as an oil even in the cold By precipitating the barium salt in the cold, the salt is obtained as a solid.

[16] Connor, Folkers and Adkins, THIS JOURNAL, 54, 1138 (1932).

[17] Reichstein, Grüssner and Zschokke, *Helv. Chim. Acta*, 15, 1066 (1932).

The Preparation of Benzoyl Hydrogen Peroxide

BY BENJAMIN T. BROOKS AND WILLIAM B. BROOKS

In the investigation of unsaturated hydrocarbons of the ethylene type by oxidation, there has been great need of a method of oxidation which will give good yields of product and which is not likely to cause rearrangement of the carbon structure Oxidation by ozone has been the most useful method, although it is difficult to prepare more than one or two grams of ozonide per day except with a very excellent ozone generator. The method of treating an olefin with benzoyl hydrogen peroxide to form the oxide, first carried out by N. Prileschajew,[1] has given excellent results in this Laboratory in the investigation of petroleum olefins and the method would undoubtedly have had much wider application except for the difficulty of preparing this reagent. L. Ruzicka, H. Silberman and M. Furter[2] have shown that this reagent reacts quantitatively with certain hydrocarbons that resist catalytic hydrogenation.

We have also found that this reagent can be used to measure the olefin unsaturation in cracked petroleum products, lubricating oils and the like, where hydrogenation is difficult or impossible due to the presence of sulfur compounds, and where the determination of iodine or bromine numbers may be unreliable.

The original method for the preparation of benzoyl hydrogen peroxide, described by Baeyer and Villiger,[3] consisted in treating an ether solution of dibenzoyl peroxide with sodium ethylate in absolute alcohol at −5°, forming ethyl benzoate and precipitating flocculent sodium perbenzoate. Water was added, the cold aqueous solution extracted several times with ether, acidified and the free acid extracted with chloroform. The yields are generally very poor, large volumes of ether are required, the extraction of the sodium salt from the ether may require several hours, and about ten to fifteen grams of the acid is all that can be expected from a good day's work. J. Lévy and M. R. Lagrave[4] improved the method somewhat by substituting toluene for ethyl ether and H. Hibbert and C. P. Burt[5] recommended adding the chilled solution of the sodium salt to a chilled excess of dilute sulfuric acid, but they erroneously attribute the poor yields so frequently obtained to the presence of free alkali in the solution. They state, "Benzoyl hydrogen peroxide is very unstable in the presence of alkali and its preparation must, therefore, be carried out in such a manner that there is no trace of sodium peroxide in solution when the free hydroperoxide is liberated." They attribute the loss of active oxygen during acidification to sodium ethylate carried into solution with the sodium salt

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(1) Prileschajew, *Ber.*, **42**, 4811 (1909); **56**, 1803, 1805, 1808 (1923); **57**, 585 (1924).

(2) Ruzicka, Silberman and Furter, *Helv. Chim. Acta*, **15**, 482 (1932).

(3) Baeyer and Villiger, *Ber.*, **33**, 1569 (1900).

(4) Lévy and Lagrave, *Bull. soc. chim.*, **37**, 1597 (1925).

(5) Hibbert and Burt, THIS JOURNAL, **47**, 2240 (1925).

and "the latter during the acidification process yields sufficient free alkali to bring about a decomposition of the hydroperoxide as fast as it is formed."

A. Baeyer and V. Villiger, in their original paper, had shown by slow or partial acidification that a sparingly soluble acid salt was formed which was exceedingly unstable. This undoubtedly accounts for the loss of active oxygen noted by Hibbert and Burt, since we have found that practically the theoretical yields of the benzoyl hydrogen peroxide were obtained by acidifying solutions containing free sodium peroxide, and also no difference could be noted in the rate of decomposition, as measured by oxygen evolution, of aqueous solutions of the sodium salt with and without free sodium hydroxide. At 0° there was no appreciable decomposition in six hours; at 25° the amount of decomposition at the end of three and one-half hours was the same in each case.

We find the benzoyl hydrogen peroxide can be made with equal facility from benzoyl chloride or dibenzoyl peroxide by treating with an excess of sodium peroxide in cold aqueous solution. No solvent is required, except a small amount of chloroform to take up the free acid after acidifying. The reaction requires very little attention, and the yield is double that obtained by the Baeyer and Villiger method or any of its later modifications. The yields show that one mole of dibenzoyl peroxide gives nearly two moles of the sodium salt of benzoyl hydrogen peroxide, evidently according to the reaction

$$C_6H_5COO_2OCC_6H_5 + Na_2O_2 \longrightarrow 2C_6H_5COO_2Na \text{ or}$$

$$Na_2O_2 + H_2O \rightleftharpoons NaOH + NaO_2H$$

$$\begin{array}{l|l} C_6H_5COO_2 & COC_6H_5 \\ + NaOH & NaO_2H \end{array} \longrightarrow 2C_6H_5COO_2Na + H_2O$$

Experimental

It was noted, in the preparation of dibenzoyl peroxide in the usual way, that the crude product contained substantial proportions of a white solid, insoluble in chloroform and readily soluble in water. This was found to be the sodium salt of benzoyl hydrogen peroxide, which changes on standing at room temperature to sodium benzoate and oxygen. It was then found that by using an excess of sodium peroxide and agitating the aqueous mixture for six hours the yield of dibenzoyl peroxide was cut down to about 20% of the theoretical, based upon the benzoyl chloride used; the balance of the material was the sodium salt of the benzoyl hydrogen peroxide, in the form of the solid, white silky needles and in solution. It was found that no loss of active oxygen occurred at 0 to +5° and that satisfactory yields could be obtained by agitating the peroxide reaction mixture for six to eight hours.

Preparation from Benzoyl Chloride.—Eighty-five grams of sodium peroxide was stirred into about 650 cc. of cracked ice and water and 100 g. of benzoyl chloride added with agitation during half an hour. The mixture, after all lumps were broken up, was kept chilled to 0 to +5°, and agitated for six hours, filtered on a chilled Buchner funnel, the solid mixture quickly transferred to 700 cc. of ice water to dissolve the finely crystalline sodium salt, filtered again and the aqueous filtrates combined. The aqueous solution was then quickly added to a slight excess of 10% sulfuric acid also chilled to about 0°. Under these conditions the benzoyl hydrogen peroxide separates, not as an oil as it does in the presence of ether and alcohol, but as a white crystalline solid. The free acid is quickly extracted with chloroform in three successive extractions. It is advantageous to add the chloroform to the sulfuric acid solution quickly so as to remove the per acid as it is liberated. The yield of the acid is readily determined by adding 5 cc. of the chloroform extract to an excess of potassium iodide solution, acidifying, and titrating the liberated iodine. In a typical experiment, as described above, the yield of dibenzoyl peroxide was 21 g. and benzoyl hydrogen peroxide 68 g. Allowing for the benzoyl chloride corresponding to the amount of dibenzoyl peroxide recovered, the yield of benzoyl hydrogen peroxide on the remaining benzoyl chloride was 91%. These results are sufficient to show that the splitting of dibenzoyl peroxide by aqueous sodium peroxide gives two moles of the sodium salt of the per acid.

The by-product dibenzoyl peroxide, which is the intermediate product in the reaction, can be employed as the original material replacing the equivalent amount of benzoyl chloride. In a typical experiment 88 g. of benzoyl chloride, 40 g. of dibenzoyl peroxide and 85 g. of sodium peroxide gave 67 g. of benzoyl hydrogen peroxide and 32 g. of dibenzoyl peroxide.

Solubility of Sodium Benzoyl Peroxide (Sodium Perbenzoate).—The solubility of the sodium salt was determined by saturating 300 cc. of water at 0° with an excess of the sodium salt, filtering quickly on a Buchner funnel and titrating a portion of the solution for active oxygen. The results show that a solution saturated with the salt at 0° contains 132 g. per liter. It was also found that the sodium benzoyl peroxide could be thrown out of its saturated solution by salting out with sodium nitrate and also by the addition of alcohol. In this connection it was surmised that perhaps the presence of alcohol in the aqueous solution of the salt, when prepared by the method of Baeyer and Villiger, caused loss of active oxygen, but alcohol was found not to be oxidized by the salt in slightly alkaline solutions at 0°. Also the addition of alcohol to chloroform solutions of the free acid resulted in no reaction at 0°.

The chloroform solutions of benzoyl hydrogen peroxide, obtained by extracting the cold aqueous solutions, are slightly cloudy from moisture, but there is not sufficient moisture present to interfere with the preparation of the oxides from unsaturated hydrocarbons. Drying by calcium chloride in the cold does not cause loss of active oxygen.

Stability of Sodium Benzoyl Peroxide.—Two small flasks each containing 100 cc. of a saturated solution of the salt were surrounded with ice and connected with gas burets. To one flask 10 cc. of 20% caustic soda was added. At the end of two and one-half hours no oxygen had been evolved from either solution.

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Mixed Benzoins. X. Conversion of Benzanisoin into Anisbenzoin

BY JOHANNES S. BUCK AND WALTER S. IDE

The only case of the direct transformation of a mixed benzoin produced by the cyanide method into its isomer, is that of the conversion of benzanisoin (α-hydroxybenzyl 4-methoxyphenyl ketone) into anisbenzoin (4-methoxy-α-hydroxybenzyl phenyl ketone).[1] Jenkins,[2] in a note just published, converts 4-methoxybenzyl phenyl ketone into the *ms*-bromo derivative and this into anisbenzoin. This conversion of benzanisoin into anisbenzoin depends on the (unusual) reduction of benzanisoin to the above ketone.[1a] Unless, therefore, a mixed benzoin can be reduced so that the CO group of the benzoin becomes the CH_2 group of the desoxy compound, the reaction is not applicable to the conversion of isomers. Few cases of such reductions are known.[1a,3] A possible route for the conversion of a mixed benzoin into its isomer depends on the course of the Tiffeneau vinyl dehydration of the hydrobenzoin.[4] In cases where this gives both desoxy compounds or where the desoxy compound formed corresponds to the exchange of the CO of the benzoin for CH_2, meso-halogenation and replacement of the halogen by hydroxyl, after the manner of Meisenheimer and Jochelson,[5] would give the isomeric mixed benzoin. A few such dehydrations have been observed.[3,4,6] Several instances of the reverse transformation are recorded (non-cyanide benzoin into cyanide benzoin) [6,7,8]

The present work was undertaken to find a general reaction capable of converting a mixed benzoin into its isomer, by an unequivocal route. Such a method has been found and it is possible to convert benzanisoin ($C_6H_5CHOHCOC_6H_4OCH_3$) into anisbenzoin ($C_6H_5COCHOHC_6H_4OCH_3$) in four simple steps. Doubtless the same series of reactions could also be used in the reverse sense, anisbenzoin to benzanisoin. The other methods which achieve this last type of change depend either on fission and recombination[1b] or on an intramolecular change of some kind.[6,7,8]

Preliminary work was carried out on benzoin itself. Benzoin was converted into benzoin-α-oxime and the oxime reduced to α-aminobenzylphenylcarbinol (diphenylhydroxyethylamine). After acetylation the product was oxidized to α-acetaminobenzyl phenyl ketone. From this, on hydrolysis, α-aminobenzyl phenyl ketone (desylamine) was obtained, and this on treatment with nitrous acid gave benzoin. The yields at each stage are good except as might be expected for the oxidation where the yield is moderate. Although benzoin itself was obtained it is clear that the CO and CHOH groups must have been interchanged.

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[1] Buck and Ide, THIS JOURNAL, **55**, 855 (1933); (a) **53**, 1536 (1931); **54**, 3012 (1932); (b) **53**, 2350 (1931); (c) **53**, 3510 (1931); (d) **53**, 1912 (1931).

[2] Jenkins, *ibid.*, **55**, 3048 (1933).

[3] Jenkins, Buck and Bigelow, *ibid.*, **52**, 4495 (1930).

[4] Orékhoff and Tiffeneau, *Bull. soc. chim.*, **37**, 1410 (1925).

[5] Meisenheimer and Jochelson, *Ann.*, **355**, 249 (1907).

[6] Jenkins, THIS JOURNAL, **53**, 3115 (1931).

[7] Luis, *J. Chem. Soc.*, 2547 (1932).

[8] Julian and Passler, THIS JOURNAL ,**54**, 4756 (1932).

An exactly similar series of reactions was carried out using benzanisoin as the starting material. There was obtained anisbenzoin identical with the compound prepared by the method of Asahina and Terasaka.[9]

Subsequent work showed that protection of the amino groups during oxidation was not essential and that the α-aminobenzylphenylcarbinol could be oxidized to the corresponding ketone directly. This observation enables two stages to be eliminated from the original series of reactions.

The reduction of the benzoin oximes to the α-aminobenzylphenylcarbinols was carried out catalytically. This means of reduction which has not previously been applied to benzoin oximes gave excellent yields in most cases and is a convenient preparative method.

The oxidation of α-aminobenzylphenylcarbinols to α-aminobenzyl phenyl ketones represents a new method of preparation for the latter compounds. The method was also applied to the α-acetaminobenzylphenylcarbinols, the corresponding α-acetaminobenzyl phenyl ketones being obtained.

The reduction (catalytic) of 2-chloro-α-hydroxybenzyl-4-methoxyphenyl ketoxime (*o*-chlorobenzanisoin oxime) presented difficulties. The major part of the chlorine was stripped from the ring and there resulted a mixture of the hydrochlorides of 4-methoxy-α-aminobenzyl-2-chlorophenylcarbinol and 4-methoxy-α-aminobenzylphenylcarbinol together with unchanged oxime and other compounds. The lability of the chlorine atom is noteworthy, and has been observed before in a similar connection.[1c]

An interesting point is that N-acetylbenzoin-α-oxime and acetylbenzil-α-oxime, on catalytic reduction, both give considerable amounts of α-acetaminobenzylphenylcarbinol. Hydrolysis or alcoholysis is apparently not involved, since the reaction also takes place in benzene solution. Probably the simplest explanation is that the acetyl group is split off during the reduction and the α-aminobenzylphenylcarbinol formed, partially reacetylated. The equations are

$$C_6H_5COC(=NOCOCH_3)C_6H_5 \longrightarrow C_6H_5CHOHCHNHCOCH_3C_6H_5 \longleftarrow$$
$$C_6H_5CHOHC(=NOCOCH_3)C_6H_5$$

The α-aminobenzyl phenyl ketones contain the group $COCHNH_2$ which often gives stable azomethylene compounds with nitrous acid.[10] No such compounds were sought for nor observed in the present work,

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(9) Asahina and Terasaka, *J. Pharm. Soc. Japan*, **494**, 19 (1923).

(10) Angeli, *Ber.*, **26**, 1715 (1893).

although they were probably intermediates in the last stage[11] of the interconversion.

Experimental

α-Aminobenzylphenylcarbinols.—The reductions were carried out in the usual Burgess-Parr apparatus, except that the bottle was heated electrically and the apparatus modified so that it could be used for 0.005 mole and upward of material;[12] 0.03 mole of the benzoin oxime, in 50 cc. of absolute alcohol, with 0.5 g. of platinum oxide (Adams) was reduced at 70–75°. The reductions were not satisfactory unless run hot. The theoretical amount of hydrogen was given in each case. The product was isolated by removing the catalyst, partially evaporating the solvent, and recrystallizing the material which separates out from the alcohol.

In the case of *o*-chlorobenzanisoin oxime, 0.04 mole (11.68 g.) was reduced in the above manner. The reduction mixture was cooled and a crop of 4-methoxy-α-aminobenzyl-2-chlorophenylcarbinol hydrochloride (2.8 g.) filtered off. The liquors were evaporated to dryness on the water-bath and the resulting crystalline mass washed well with ether; 3.9 g. of 4-methoxy-α-aminobenzylphenylcarbinol hydrochloride was so obtained. The remainder of the starting material was accounted for as unchanged, together with other compounds not identified. The bases were liberated from the aqueous solutions of the hydrochlorides by sodium hydroxide. The reduction of the acetyl oximes was carried out in a similar manner but at room temperature.

TABLE I

α-AMINOBENZYLPHENYLCARBINOLS AND DERIVATIVES

	Compound reduced	Product, phenylcarbinol	Yield, %	M. p., °C.
1	Benzoin-α-oxime[13]	α-Aminobenzyl-	86	
2	Benzil-α-monoxime[14]	α-Aminobenzyl-	85	
3	Acetyl benzoin-α-oxime[13]	α-Acetaminobenzyl-	19	197
4	Acetyl benzil-α-monoxime[15]	α-Acetaminobenzyl-	19	
5	Benzanisoin oxime[1d]	4-Methoxy-α-aminobenzyl	66	123
6	Dimethylaminobenzoin oxime[1d]	4-Dimethylamino-α-aminobenzyl-	80	151
7	*o*-Chlorobenzanisoin oxime[1d]	Hydrochloride of 4-methoxy-α-aminobenzyl-	35	233 dec.
8	*o*-Chlorobenzanisoin oxime[1d]	Hydrochloride of 4-methoxy-α-aminobenzyl-2-chloro-	22	252 dec.
9	(From salt)	4-Methoxy-α-aminobenzyl-2-chloro-	..	115

	Solvent	Appearance	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3	Alcohol	Glittering small needles	75.25	74.91	6.71	6.43
5	Alcohol	Flat rect. prisms	74.03	74.09	7.04	7.05
6	Alcohol	Small stout prisms	74.95	75.04	7.86	7.75
7	Alcohol	Tiny jagged needles	64.38	64.20	6.49	6.68
8	Alc.-ether	Felted hair-like needles	57.32	57.56	5.45	5.31
9	Aq. alcohol	Small stout prisms	64.84	65.20	5.80	5.96

Acetylation of α-Aminobenzylphenylcarbinols.—The N-acetylation was accomplished readily by treating the carbinol with 2.5 times its weight of acetic anhydride.

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(11) *Cf.* Schroeter, *Ber.*, **42**, 2345 (1909).

(12) Buck and Jenkins, THIS JOURNAL, **51**, 2163 (1929).

(13) Werner and Detscheff, *Ber.*, **38**, 69 (1905).

(14) Taylor and Marks, *J. Chem. Soc.*, 2305 (1930).

(15) Auwers and Meyer, *Ber.*, **22**, 545 (1889).

Heat was evolved and the mass solidified. After heating for ten minutes on the water-bath, the mixture was cooled, allowed to stand in the cold, ether added, and the product filtered off and recrystallized from alcohol. The compounds (except the *o*-chloro compound) are sparingly to moderately soluble in hot alcohol. The *o*-chloro compound is rather soluble in alcohol.

In the acetylation of α-aminobenzylphenylcarbinol, some α-acetaminobenzylphenylcarbinol acetate is usually produced. It melts at 219° (lit. 213°) and was checked against an authentic specimen.[16]

4-Methoxy-α-acetaminobenzyl-2-chlorophenylcarbinol, on account of its greater solubility, is best isolated by pouring the reaction mixture into water, and, after warming, allowing the mixture to stand in the cold.

TABLE II

α-ACETAMINOBENZYLPHENYLCARBINOLS

	Compound, phenylcarbinol	Solvent	Yield, %	M. p., °C.	Appearance	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	α-Acetaminobenzyl-[16]	Alcohol	79	197	Glittering small needles	75.25	74.91	6.71	6.43
2	4-Methoxy-α-acetaminobenzyl-	Alcohol	91	183	Felted tiny needles	71.54	71.57	6.72	6.87
3	4-Methoxy-α-acetaminobenzyl-2-chloro-	Aq. alcohol	79	122	Small thick prisms	63.83	64.00	5.67	5.99
4	4-Dimethylamino-α-acetaminobenzyl-	Alcohol	94	187	Glittering felted needles	72.44	72.48	7.44	7.59

α-Acetaminobenzyl Phenyl Ketones (Acetyldesylamines.)—The α-acetaminobenzylphenylcarbinol was dissolved in four times its weight of acetic acid. A solution of chromic acid (= one O) in a little aqueous acetic acid was added in portions. The temperature at the start was 40° and after the addition 70°. The mixture was kept at 70° for ten minutes, allowed to cool, and gradually diluted in the refrigerator. The product which separated was filtered off and fractionated from alcohol until pure.

α-Aminobenzyl Phenyl Ketones (Desylamines).—The oxidation of the (unacetylated) α-aminobenzylphenylcarbinols was carried out in dilute sulfuric acid solution, using chromic acid (= one O). For the unsubstituted carbinol 7 parts of 20% sulfuric acid were used and for the methoxy carbinol, 12 parts. After mixing at about 40° the reaction mixture was slowly (twenty minutes) heated to 70°. α-Aminobenzyl phenyl ketone readily separates as sulfate on adding further sulfuric acid to the mixture; yield, 59% as base, via the sulfate.

4-Methoxy-α-aminobenzyl phenyl ketone cannot be separated as sulfate. The oxidation mixture was therefore extracted with ether to remove non-basic material, made alkaline with ammonia, extracted with ether (very troublesome), the extract dried over anhydrous sodium sulfate, and the solution treated with hydrogen chloride. The hydrochloride which was precipitated was filtered off and dried *in vacuo*. The yield was 70% as hydrochloride, via the base. The free 4-methoxy-α-aminobenzyl phenyl ketone rapidly turns yellow when removed from solvent, and undergoes some change. For this reason a pure specimen was not isolated. The hydrochloride, however, is quite stable.

The same α-aminobenzyl phenyl ketones are obtained by the hydrolysis of the α-acetaminobenzyl phenyl ketones. For the unsubstituted compound (acetyldesylamine) digestion on the bath with eight times its weight of concd. hydrochloric acid for 3.6 hours

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(16) Söderbaum, *Ber.*, **29**, 1210 (1896).

was found best. The yield was 91% (as hydrochloride). In the case of the methoxy compound much difficulty was encountered with hydrochloric acid. Ultimately it was found that refluxing for four and one-half hours with sulfuric acid (1 vol concd sulfuric acid to 5 vols. water) gave good results. The yield (isolated as hydrochloride via the base) was 92%.

TABLE III

α-ACETAMINOBENZYL PHENYL KETONES AND α-AMINOBENZYL PHENYL KETONES

	Compound, benzyl phenyl ketone	Solvent	Yield, %	M. p., °C.
1	α-Acetamino-	Aq. alcohol	52	132
2	4-Methoxy-α-acetamino-	Aq. alcohol	37	112
3	4-Methoxy-α-amino-	Ether	..	soft 88 froth 94
4	Hydrochloride of α-amino-[17]	Alc.-ether	91	245 yellow, froth
5	Hydrochloride of 4-methoxy-α-amino-	Alcohol	92	236 orange, froth

	Appearance	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	Glittering flat needles	75.85	75.75	5.96	6.01
2	Dull white nodules of tiny needle prisms	72.05	72.04	6.05	6.14
3	Yellow crust of tiny spheres	Nitrogen	calcd.,	5.80.	found, 5.81
4	Bundles of thick glassy needles	67.86	67.81	5.70	5.92
5	Clusters of tiny jagged needles	64.85	65.09	5.81	6.02

Benzoin from α-Aminobenzyl Phenyl Ketone.—2.7 g. of α-aminobenzyl phenyl ketone hydrochloride was dissolved in 40 cc. of water, cooled, and 3.0 cc. of concd. hydrochloric acid added. A solution of 1.4 g. of sodium nitrite (2 moles) in 15 cc. of water was then added in portions at room temperature. The mixture was warmed on the bath for a few minutes until the nitrogen was expelled. The yellowish oil which separated solidified on cooling and was filtered off; yield 91%. After recrystallization the product was pure white and was identified as benzoin (checked against authentic benzoin).

Anisbenzoin from 4-Methoxy-α-aminobenzyl Phenyl Ketone.—The reaction was carried out substantially as above, except that 8 cc. of concd. sulfuric acid was used in place of the 3 cc. of concd. hydrochloric acid and stronger heating was required to drive off the nitrogen. The oily product was extracted with ether, the ether evaporated, and the oil taken up in dilute alcohol. The anisbenzoin crystallized out on standing in the cold. It was checked, after recrystallization, against an authentic specimen.[9] For confirmation, it was oxidized (Fehling's solution) to benzanisil and this was then checked against an authentic specimen. The yield of anisbenzoin (crystalline) was about 50%, but this must be considered as minimal on account of the difficulty of crystallizing the compound in the presence of impurities.

It is not necessary to isolate the α-aminobenzyl phenyl ketones or their salts from the hydrolysis mixtures, as these can be treated (after extraction with ether) directly with sodium nitrite.

When the unacetylated compounds are oxidized, the oxidation mixture may, after extraction with ether, be treated directly with sodium nitrite and then heated. The resulting benzoin is extracted with ether. The cold liquors, treated with a second portion of sodium nitrite and again heated, give a further amount of the benzoin.

Summary

1. A series of reactions is described whereby benzanisoin was converted into anisbenzoin. The reactions can probably be applied to other

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(17) Pschorr and Brüggemann, *Ber.*, **35**, 2740 (1902).

mixed benzoins. Benzoin itself as starting material gave benzoin as the end product.

2. An expeditious method for the preparation of α-aminobenzylphenylcarbinols is the catalytic reduction of the oximes of benzoins.

3. α-Aminobenzyl phenyl ketones are produced by the oxidation of α-aminobenzylphenylcarbinols.

4. α-Acetaminobenzyl phenyl ketones are produced by the oxidation of α-acetaminobenzylphenylcarbinols. The acetyl group may be removed by hydrolysis.

5. In the catalytic reduction of 2-chloro-α-hydroxybenzyl-4-methoxyphenyl ketoxime, the chlorine is largely split from the nucleus.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminum Chloride. VI. Condensation of Phenylpropylcarbinol and α-Chlorobutylbenzene with Phenol

BY RALPH C. HUSTON AND HAROLD W. STRICKLER

The work here described may be considered a continuation of that with Lewis and Grotemut[1] on the condensation of secondary alcohols with phenols.

The phenylpropylcarbinol used was prepared from propyl bromide and benzaldehyde by the Grignard reaction. A yield of 81% was obtained when the reactants were used in the proportion of one of propyl bromide to one of magnesium to four-fifths of benzaldehyde[2,3] and when the reaction mixture was cooled to a slight visible reaction during the preparation of the Grignard reagent and in ice during the addition of the benzaldehyde.[4] Because of the lack of agreement[5] as to the boiling point and density of this compound these constants were carefully redetermined: b. p. 94–96° (6 mm.), sp. gr. 18/4°, 0.974.

Condensation of one mole of phenylpropylcarbinol (or α-chlorobutylbenzene) with one mole of phenol in petroleum ether at 20–25°, by means of one-half mole of aluminum chloride,[6] gave a 20% yield of 4-(α-phenylbutyl)-phenol and a 6% yield of 2-(α-phenylbutyl)-phenol. These were separated by repeated fractionation at reduced pressure. Solution of the crude product in Claisen's alcoholic potassium hydroxide and extraction with petroleum ether gave no evidence of the formation of α-phenylbutyl phenyl ether (see table).

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[1] Huston, Lewis and Grotemut, THIS JOURNAL, 49, 1365 (1927).

[2] Meisenheimer, *Ann.*, 442, 180 (1925).

[3] Gilman and McCracken, THIS JOURNAL, 45, 159 (1923).

[4] Rheinboldt and Roleff, *J. prakt. Chem.*, 109, 175 (1925).

[5] Marshall and Perkin, *J. Chem. Soc.*, 59, 885 (1891); Grignard, *Chem. Centr.*, II, 7622 (1901); Klages, *Ber.*, 37, 2312 (1904); Puyal and Montague, *Bull. soc. chim.*, 27, 857 (1920); Strauss and Grindel, *Ann.*, 439, 276, 312 (1924).

[6] Huston, THIS JOURNAL, 46, 2777 (1924).

Condensation of α-chlorobutylbenzene[7] with phenol by Claisen's method[8] gave a 13% yield of 2-(α-phenylbutyl)-phenol, a 12% yield of phenylbutylene[9] and a 10% yield of α-phenylbutyl phenyl ether. The last two products were obtained by fractionation of the petroleum ether extract of the alcoholic potassium hydroxide solution.

Bromination of 4-(α-phenylbutyl)-phenol in cold chloroform with two moles of bromine gave 4-(α-phenylbutyl)-2,6-dibromophenol. This was also produced by condensing phenylpropylcarbinol with 2,6-dibromophenol by means of aluminum chloride.

The preparation of 2-(α-phenylbutyl)-4,6-dibromophenol was effected either by bromination of the substituted phenol or from 2,4-dibromophenol by the Claisen reaction.

Esters were prepared by the pyridine method.[10]

TABLE I

Compound	Physical appearance	Empirical Formula	M. p. or b. p., °C.	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found	
4-(α-Phenylbutyl)-phenol	Mats of fine silky threads from pet. ether. (Shows tendency to swell and retain solvent)	$C_{16}H_{18}O$	M 49–50; B 154–155 (6 mm.)	84.91	84.89	84.64	8.02	7.97	7.94
2-(α-Phenylbutyl)-phenol	Viscous oil	$C_{16}H_{18}O$	B 144–146 (6 mm.)	84.91	84.61	84.70	8.02	8.025	8.065
α-Phenylbutyl phenyl ether	Mobile colorless liquid (sp. gr. at 25°/4° 1.0067, n_{20} 1.5507)	$C_{16}H_{18}O$	B 123–125 (6 mm.)	84.91	84.77	84.76	8.02	8.01	7.96
4-(α-Phenylbutyl)-2,6-dibromophenol	Viscous oil	$C_{16}H_{16}OBr_2$	B 188–189 (6 mm.)	Br, 41.63	41.49				
2-(α-Phenylbutyl)-4,6-dibromophenol	Viscous oil	$C_{16}H_{16}OBr_2$	B 184–185 (6 mm.)	Br, 41.63	41.36				
Benzoyl ester of 4-(α-phenylbutyl)-phenol	Monoclinic crystals	$C_{23}H_{22}O_2$	M 70–71	83.58	83.4		6.71	6.76	

The benzoyl, benzene sulfonyl and *p*-toluene sulfonyl esters of 2-(α-phenylbutyl)-phenol were heavy oils which failed to crystallize.

EAST LANSING, MICHIGAN

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[7] This was prepared from the pure alcohol. It boiled at 73–75° (6 mm.) and had a sp. gr. at 18/4° 1.0182. *Cf.* Klages, *Ber.*, **37**, 2312 (1904).

[8] Claisen, *Ann.*, **442**, 210 (1925).

[9] Radziszewski, *Ber.*, **9**, 260 (1876).

[10] Einhorn and Holland, *Ann.*, **301**, 95 (1898).

[CONTRIBUTION NO. 136 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

The Molecular Weight of Linear Macromolecules by Ultracentrifugal Analysis. I. Polymeric ω-Hydroxydecanoic Acid[1]

BY E. O. KRAEMER AND W. D. LANSING

The most satisfactory results for the molecular weights of macromolecules have been obtained for the proteins by Svedberg and his associates using the ultracentrifuge.[2]

The proteins, however, appear to be exceptional among the macromolecular colloids, for, as shown by the viscosity and ultracentrifugal behavior of their solutions, many of them obey the kinetic theory for spherical particles reasonably well. Presumably, therefore, the dissolved units are nearly spherical in shape. On the other hand, macromolecular colloids in general display an anomalous behavior, which is particularly evident in connection with viscosity and with diffusion. For example, the specific hydrodynamic volume, calculated from viscosity,[3] may be many times greater than the specific volume of the colloid. Chemical and physical evidence indicates that the macromolecules in many cases exist in solution as highly elongated, perhaps rod-like, perhaps string-like units, and, as has been pointed out,[4] diffusion and sedimentation methods for molecular weight might be expected to give erroneous results. In order, therefore, to test the applicability of the ultracentrifugal methods to macromolecular colloids in general, an empirical study of the behavior of long-chain molecules was carried out with a particularly well-defined synthetic macromolecular substance of simple structure and known molecular weight.

The substance selected was a highly polymerized ω-hydroxydecanoic acid prepared and described by Carothers and Van Natta.[5] From chemical evidence it is practically certain that polymerization in this case involves self-esterification, with the formation of a linear polymer having the formula $HO-[(CH_2)_9-CO-O]_x-H$. The terminal carboxyl is the only acid group in the molecule. Consequently, the acid equivalent is equal to the molecular weight, which is thus determinable by titration with alkali. The specimen used in this investigation has a molecular weight, by titration, of 25,200; *i. e.*, the molecule consists of a chain of about 150 hydroxydecanoic acid residues. A study of the viscosity of solutions of this polymer as well as polymers of lower molecular weight in *sym*-tetrachloro-

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(1) Presented at the Denver Meeting of the American Chemical Society, August, 1932.

(2) See, for instance, Svedberg, "Colloid Chemistry," A. C. S. Monograph, Chemical Catalog Co., New York, 2d ed., 1928, and many papers in THIS JOURNAL, 1923–1933.

(3) Kraemer, Chap. XX, in Taylor's "Treatise on Physical Chemistry," 2d ed., 1931, p 1615.

(4) Kraemer and Sears, *J. Rheology*, 1, 238 (1930).

(5) Carothers and Van Natta, THIS JOURNAL, in press.

ethane has already been published by Kraemer and Van Natta,[6] who showed that the synthetic polyester resembles the high-viscosity type of intrinsic colloid rather than the simpler proteins.

Solutions of the polymer in *sym*-tetrabromoethane were subjected to ultracentrifugal analysis under conditions suitable for measuring diffusion, sedimentation velocity, and sedimentation equilibrium, and molecular weights were calculated in the usual way. Briefly, it was found that the molecular weight by the sedimentation-equilibrium method checked that by titration, whereas diffusion gave too large a value and sedimentation velocity gave too small a value. Calculation of the relation between osmotic pressure and concentration from the sedimentation equilibrium showed that van't Hoff's equation is not obeyed at concentrations exceeding 0.2% by weight or 0.00024 normal.

Experimental Details and Results

The ultracentrifuge used in this work was built under the direction of Professor Svedberg at the University of Upsala, and has been described by Svedberg and Sjögren.[7] The concentration gradients were determined by means of the refractive-index method, and the calculations were carried out in accordance with the methods developed in Svedberg's laboratory.[8]

The tetrabromoethane used as solvent was obtained from the Dow Chemical Co. Its physical properties were as follows: d_4^{20} 2.9596, refractive index $n_{436}^{20.7}$ 1.6598. The partial specific volume of the solute over the concentration range in question was determined pycnometrically and was found to be 1.013. The relation between refractive index and concentration, required in determining concentration gradients in the centrifuging cell, was established by measurements with the Pulfrich refractometer. dn/dc, the rate of change in refractive index with concentration in weight per cent., was 0.00577 for a wave length of 436 mμ.

Figure 1 presents experimental data for one run, the successive curves representing conditions during centrifuging at six-hour intervals. The position of the maximum locates the mean position of the boundary of the solute molecules as they move from the end of the cell, and from the rate of shift of the maximum, the sedimentation velocity is calculated. As the boundary moves, it becomes less sharp, owing to diffusion, and the width of the peak increases and its height decreases. From the rate at which this occurs, the diffusion coefficient is calculated. The maximum height of Curve D on Fig. 1 is labeled $Z_{\text{max.}}$. A height h from the bottom is laid off such that $h = Z_{\text{max.}}/\sqrt{e} = 0.606\ Z_{\text{max.}}$ The half-width of the curve u at this height is connected with the diffusion coefficient D by the equation

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[6] Kraemer and Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).

[7] Svedberg and Sjögren, THIS JOURNAL, **51**, 3594 (1929).

[8] Lamm, *Z. physik. Chem.*, **A138**, 313 (1928); **A143**, 177 (1929); Stamm, THIS JOURNAL, **52**, 3047 (1930).

$Dt = u^2/2$, where t is the time in seconds from the start of the run. In passing, it may be noted that the solute sedimented toward the center of rotation on account of the higher density of the solvent, contrary to the case for most ultracentrifugal investigations hitherto published.

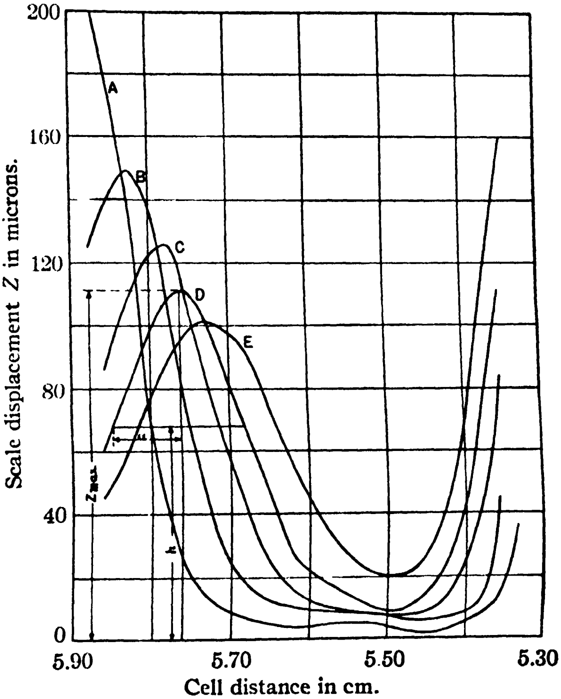

Fig. 1.—Curve A, 6 hours; Curve B, 12 hours; Curve C, 18 hours; Curve D, 24 hours; Curve E, 30 hours.

The values of the specific sedimentation velocity and the diffusion coefficient are given in Table I. From the former the apparent radius of the molecule, considered as a sphere, and the apparent molecular weight were calculated by means of Stokes's equation. Similarly, by means of Einstein's equation for the diffusion of spherical particles, an apparent molecular weight was calculated from the diffusion coefficient. A molecular weight value was also obtained by combining diffusion and sedimentation constants, as Svedberg and his associates commonly do, on the assumption that the frictional resistance offered by the liquid is the same for both cases. For this purpose the equation $M = RTs/D(1 - V\rho)$ is used. These various apparent molecular weights are also given in Table I.

The results for a sedimentation equilibrium run are shown graphically by Fig. 2, Curve I, representing an average of the displacements observed on the fifth, sixth and seventh days of centrifuging. The average devia-

TABLE I

ULTRACENTRIFUGAL ANALYSIS OF ω-HYDROXYDECANOIC ACID POLYMER IN *Sym*-TETRABROMOETHANE

	Expt. HDA-1	Expt. HDA-10	Expt. HDA-10 (corr. to 20°)
Temperature, °C.	20.2	40.2	....
Concentration, wt. %	0.199	0.108	....
Speed for sedimentation velocity (r. p. m.)	8600	12,000	....
Centrifugal force (× gravity)	4500	8900	....
Viscosity of solvent in poises	0.105	0.055	0.105
Relative viscosity of solution in tetrachloroethane[6]	1.63	1.25	....
Specific sedimentation velocity	6.98×10^{-14}	1.65×10^{-13}	8.65×10^{-14}
Diffusion coefficient (cm.^{2}/sec.)	1.33×10^{-8}	4.13×10^{-8}	2.03×10^{-8}
Molecular weight from diffusion coeff.	8,400,000	2,400,000	....
Molecular weight from sed. velocity	5400	7600	....
Mol. wt. from sed. vel. + diff.	64,000	52,000	....
Mol. wt. from sed. equil. (speed 7200 r. p. m.)	....	27,000	....
Mol. wt. from combining wt.	25,200	25,200	....
Mol. wt. from viscosity (Staudinger's method)[6]	....	31,000	....

tion of individual points from this curve is of the order of one or two microns, with a maximum deviation of about 5 microns. The broken portions of the curve at either end are calculated scale displacements for a molecular weight of 26,000, which agrees with the solid curve in the center portion. Comparisons on a large-scale graph of calculated curves for molecular weights 26,000 and 28,000 and the observed data show that the

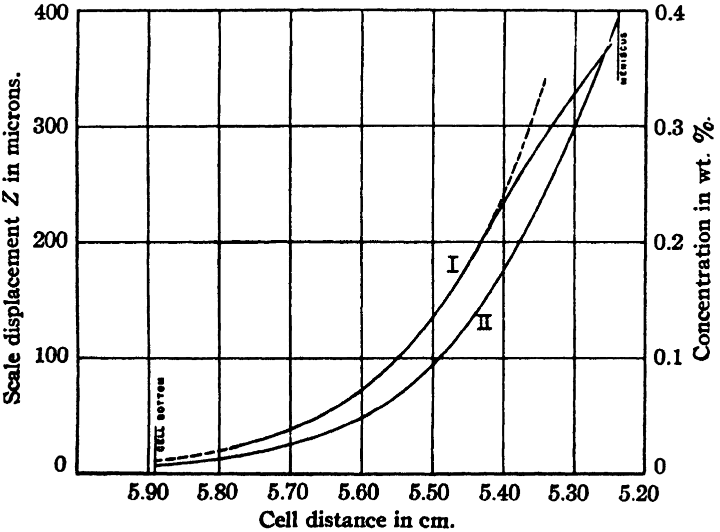

Fig. 2.—I, Scale displacement curve. II, concentration curve.

most probable molecular weight is about 27,000, and that figure has been included in Table I.

Discussion

Variation in Molecular Weights.—Upon comparison of the results in Table I, it is immediately evident that the different methods gave grossly different values for the molecular weight. Only the sedimentation-equilibrium value agrees with the combining weight. The molecular weight by diffusion is much too high, and the molecular weight by sedimentation velocity is too low.

As was pointed out above, all these values were calculated by means of equations for ideal cases, which for diffusion and sedimentation velocity are definitely restricted to spherical particles. The theory for sedimentation equilibrium indicates that it does not depend upon particle or molecular shape. Although the exact equations have not been worked out for non-spherical particles, it is known that departure from spherical form increases the frictional resistance of a particle of given volume moving through a viscous medium. Molecular weight values for such cases, calculated from diffusion by the equation for spherical particles, are therefore inevitably anomalously high, and values calculated from sedimentation velocity are inevitably anomalously low. The assumption of the same frictional coefficient for both cases, which amounts to solving the diffusion and sedimentation equations simultaneously for both frictional coefficient and molecular weight, equally inevitably gives an intermediate value of the molecular weight, which might be expected to be nearer the true value than the values from either diffusion or sedimentation velocity alone. In the light of these facts we may conclude that the hydroxydecanoic acid polymer is dispersed in solution as single molecules, and that the correct molecular weight is obtained by the sedimentation-equilibrium method. The molecule is far from spherical in form, and, therefore, its weight (or size) cannot be determined from the diffusion coefficient or the sedimentation velocity. At the concentrations studied, the friction coefficient is not the same for diffusion and sedimentation velocity, and the molecular weight cannot be determined by combining them, as is possible for spherical or near-spherical molecules. For instance, at 0.108% concentration, the friction corresponding to the diffusion coefficient ($f_D = RT/DN$) is about 4.5 times that for a spherical molecule of the same volume (*e. g.*, egg albumin), whereas the friction corresponding to the sedimentation constant [$f_S = (1 - V\rho)/s$] is 2.2 times that for a spherical molecule. The latter ratio is called by Svedberg the "Dissymmetry Number,"[9] and it indicates a degree of dissymmetry very much greater than any yet found among proteins of comparable molecular weight.

As shown by the data of Table I, the friction coefficients for both dif-

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(9) Svedberg and Eriksson, THIS JOURNAL, 54, 4737 (1932).

fusion and sedimentation velocity increase with concentration, the more rapid change occurring for diffusion. Similar observations were made by Stamm in his ultracentrifugal analysis of cellulose.[10] Since viscous friction of the solution is a linear function of concentration, one might expect the friction coefficients to be linear functions of concentration. At any rate, linear extrapolation of the two pairs of values provided by Table I to zero concentration gives a common intercept on the friction axis at $f_D = f_S = 7.03 \times 10^{-7}$, which is 1.6 times that for a spherical molecule of the same volume. Calculation of the corresponding diffusion coefficient and sedimentation constant for zero concentration gives values of 5.70×10^{-8} and 1.19×10^{-13}, respectively. Calculation of the molecular weight from these two values, on the basis of equal friction coefficients, gives a value of 26,000, in good agreement with the value from sedimentation equilibrium. Admittedly more detailed data will be required to prove definitely whether this is the proper way of correcting for the effect of concentration upon the diffusion coefficient and the sedimentation velocity.

An important question in judging the validity of the conclusions and inferences stated above concerns the homogeneity of the polymer with respect to molecular weight. It is, however, somewhat difficult to characterize this feature in a quantitative manner. Scale-displacement curves have been calculated for a uniform sample of molecular weight 26,000, and for a hypothetical mixture consisting of 50% molecular weight 26,000, and 25% each of 20,000 and 32,000 molecular weight, but on the scale of Fig. 2 the two curves would not be distinguishable. The sample, therefore, might be at least as inhomogeneous as the hypothetical mixture. The sedimentation velocity and diffusion curves (Fig. 1) appear to show that the sample is uniform. For a non-uniform sample, the peaks shown in Fig. 1 broaden out with time due to the combined effect of diffusion and the separation of the different particle sizes. Since there is no detectable drift in the diffusion coefficient, the observed broadening of these curves appears to be entirely accounted for by the diffusion. On the other hand, due to the non-spherical shape of the molecule, we are not able to calculate the sensitiveness of this effect as a measure for uniformity. In the absence of more sensitive tests for uniformity (perhaps sedimentation velocity with a very high centrifugal force), all that we can say with assurance is that this sample presents no evidences of marked non-homogeneity.

Osmotic Pressure vs. Concentration.—It may be seen in Fig. 2 that the experimental curve at one end falls distinctly lower than the theoretical curve for a homogeneous material, and at first sight it might appear that this represents some anomalous condition. By expressing the data in another form, however, it may be shown that the anomaly is of a sort frequently displayed by solutions of intrinsic colloids.

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[10] Stamm, This Journal, 52, 3047 (1930).

Thermodynamically, the measurement of sedimentation equilibrium is equivalent to the determination of the osmotic pressure. Tiselius[11] has shown how the activity of the solvent or the solute may be calculated for any point in the centrifuge cell at sedimentation equilibrium. The corresponding osmotic pressures can be calculated by the usual methods.[12] Thus the relation between osmotic pressure and concentration can be determined for the range of concentrations represented in the sedimentation equilibrium. Curve II, Fig. 2, represents the variation in concentration with cell-distance at equilibrium, as calculated by integration from Curve I, using Lamm's equation ($Z = Gab(\mathrm{d}n/\mathrm{d}x)$), and the experimentally determined value of $\mathrm{d}n/\mathrm{d}c$ expressing the relation between refractive index and concentration. By integration of Curve II one obtains the amount of centrifugible solute in the cell, which in this particular case corresponded to 98% of the total solute present at the beginning of the run.

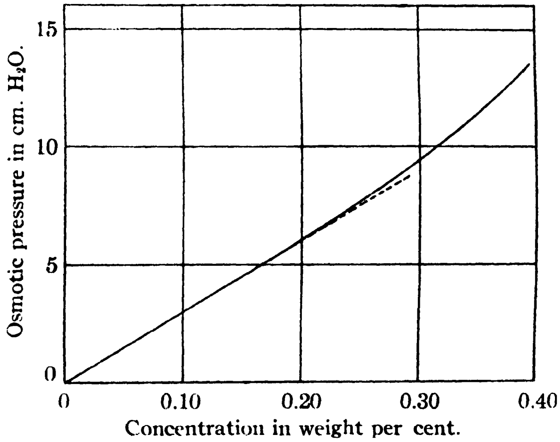

Fig. 3.

From Curve II of Fig. 2, the solid curve of Fig. 3, representing the empirical relation between osmotic pressure and concentration, was calculated. The broken curve is a straight line, corresponding to van't Hoff's equation for a molecular weight of 27,000. It is evident that the sedimentation equilibrium "anomaly" can be interpreted as due to a deviation from the laws of ideal dilute solutions at concentrations higher than about 0.2% by weight or 0.00024 normal. Such behavior has frequently been observed in the osmotic behavior of intrinsic colloids.[13] The viscosity–concentration data for the same polymer also show a departure from linearity above 0.2%.[6]

(11) Tiselius, *Z. physik. Chem.*, **124**, 449 (1926).

(12) Lewis and Randall, "Thermodynamics," New York, 1923, p. 213.

(13) Freundlich, "Kapillarchemie," 4th ed., 1932, Vol. II, p. 321; Grard, *J. chim. phys.*, **29**, 287 (1932).

Comparison of Viscosity, Diffusion and Sedimentation.—Non-ideal behavior in diffusion and sedimentation is probably due to the same structural features that give rise to non-ideal viscous behavior. The results of this investigation confirm the suggestion of Kraemer and Sears[4] that ultracentrifugal analysis should be carried out at concentrations sufficiently low to give a linear relationship between relative viscosity and concentration, and that even under these conditions, diffusion and sedimentation may be expected to be anomalous whenever the ratio of the specific hydrodynamic volume to the partial specific volume of the solute is much greater than unity. For the case in question, this ratio is 74. The apparent specific volume, calculated from diffusion on the assumption of a spherical molecule, is about 90 times the partial specific volume, so it would seem that the hydrodynamic conditions associated with flow and diffusion are closely related. For sedimentation velocity, the apparent specific volume is only eleven times the actual volume at 0.1% concentration. Detailed study of these interrelations and the influence of concentration probably would give considerable information concerning molecular shape, and perhaps would answer the question as to whether a linear macromolecule in solution is approximately straight or is more or less coiled up.

We wish to acknowledge our indebtedness to Professor The Svedberg for the opportunity of discussing our results with him.

Summary

Polymeric ω-hydroxydecanoic acid, a typical high-viscosity type of linear macromolecular colloid, has been subjected to ultracentrifugal analysis. The molecular weight calculated from sedimentation equilibrium agreed with the chemical value, and is believed to be correct. Diffusion coefficient gave much too high a molecular weight, whereas sedimentation velocity gave much too low a value. According to the osmotic pressure *vs.* concentration relations, as calculated from the sedimentation equilibrium, van't Hoff's law does not apply at concentrations exceeding 0.00025 normal. It is believed that rubber, cellulose and cellulose derivatives and similar macromolecular colloids would show a similar behavior.

WILMINGTON, DELAWARE

RECEIVED AUGUST 7, 1933
PUBLISHED OCTOBER 6, 1933

Notes

Note on an Improved Laboratory Ozonizer

By Lee Irvin Smith and Glenn E. Ullyot

Some years ago one of us[1] published a description of a convenient laboratory ozonizer capable of giving high concentrations of ozone. Recently the original ozonizer was rebuilt and simplified, and since requests for details regarding the machine have come to us frequently, we are publishing a short description of the new machine.

The new tubes have the same dimensions as the old ones, except that the upper collar (Fig. 1, Ref. 1, p. 1845) marked "litharge cement" instead of being 2.7 cm. is about 10 cm. high, and the inner core and the mercury filling have been dispensed with. This collar carries a cork stopper, through which passes a short piece of glass tubing, and the copper wire from the secondary of the transformer passes through this piece of tubing and reaches nearly to the bottom of the ozonizing tube. The inner tube is filled with distilled water, the three ozonizing tubes are connected in series through mercury seals and the whole assembly set in the large battery jar which then is filled with distilled water. During operation, the temperature of the water in the inner tube rises a few degrees in the course of two or three hours, but the temperature of the outer bath of water remains practically constant even when the machine is run continuously for long periods of time.

We first tried making the new tubes of thin-walled Pyrex glass, but to our astonishment, these tubes sparked continuously and gave almost no "silent discharge," with the result that very little ozone was produced. We tried reducing the voltage in the primary of the transformer, and also changing the distance between the inner and outer tubes, but in all our experiments one of two things invariably happened: either no current at all passed, or else there was sparking, and in none of our experiments with Pyrex were we able to get more than about 2% ozone. We therefore returned to soft glass as the material out of which to construct the tubes.

The general assembly, details of analysis, procedure, etc., were the same as those described in the original paper. Using three tubes in series, 0.055 Kva transformer wound 88 to 1 and taking 110 volts in the primary, the new machine, with dry oxygen, gives from 4.5 to 7.0% ozone by volume (6.7 to 10.0% by weight) when the gas is passing at rates of 19 and 6.5 liters per hour, respectively.

Finally, we have eliminated the hot tube ozone "destroyer" used in connection with the older work, because, when using inflammable solvents, the exit gases occasionally became ignited in the destroyer and struck back into the reaction apparatus. If the exit gases are passed through two towers filled with broken glass and moistened with 5% sodium hydroxide solution, practically all the ozone is destroyed, and this is a much safer way of destroying the excess ozone than the hot tube–manganese dioxide method previously used.

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[1] Smith, This Journal, 47, 1844 (1925).

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

RECEIVED JULY 28, 1933
PUBLISHED OCTOBER 6, 1933

The Thermal Decomposition of Lead Tetraphenyl

BY MALCOLM F. DULL AND J. H. SIMONS

The quantitative production of diphenyl from lead tetraphenyl has been reported by Zartman and Adkins.[1] They state that both the presence of nickel as a catalyst and hydrogen at high pressure (100 atmospheres) were necessary in this reaction at 200°. We have found, however, that a quantitative yield of diphenyl could be obtained at a somewhat higher temperature, 252°, and in the absence of hydrogen or other gas and without the addition of catalyst.

We have studied the thermal decomposition of lead tetraphenyl over a range of temperature in sealed Pyrex bulbs, which were carefully evacuated after the introduction of the lead tetraphenyl. The technique was similar to that used by Simons, McNamee and Hurd[2] in their work on the static decomposition of lead tetramethyl.

The lead tetraphenyl used had been prepared in the usual way from phenylmagnesium bromide and lead chloride and purified by crystallization from hot benzene. It was a white crystalline substance with a melting point of 223°.

The data which we have obtained are given in the table of results. The yield of diphenyl is smaller as the temperature used is higher, and benzene and *p*-diphenylbenzene are both formed at the higher temperatures.

TABLE OF RESULTS

Run number	1	2	5	6	7	3	4
Temperature, °C.	252	345	400	400	450	450–460	550
Time, minutes	135	130	60	80	45	30	20
Sample, g.	2.1	2.0	3.0	3.0	3.0	2.0	2 0
Lead tetraphenyl recov., g.	0.0	0.1	0.19	0.22	0.24	0.68	...
Lead tetraphenyl dec., g.	2.1	1.9	2.81	2.78	2.76	1 32	..
Benzene obtained, g.	0.0	..	0.39	0.40	0.21	..	..
p-Diphenylbenzene obtained, g.	0.0	0.57	.13	.16	.05	...	...
Diphenyl obtained, g	1.3	.57	.77	.47	37	...	.
Yield of diphenyl, %	100	50	46	28	22	..	..

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(1) Zartman and Adkins, THIS JOURNAL, **54**, 3398 (1932).

(2) Simons, McNamee and Hurd, *J. Phys Chem.*, **36**, 939 (1932).

Remarks.—Unpurified diphenyl from run 1 had a melting point of 69–69.5°. The temperature of 252° was the lowest at which observable decomposition took place. The lead deposit in run 1 was bright. All other runs exhibited more or less charring. In runs 2 and 6 the bulb was placed in the cold furnace and then rapidly heated. In the other runs the bulb was placed in a hot furnace. The benzene was determined by the difference in weight caused by passing a stream of air through the bulb. These values are probably high, due to the volatility of diphenyl. The undecomposed lead tetraphenyl was recovered by precipitation with acetone, and the *p*-diphenylbenzene and diphenyl separated by solution in ethyl alcohol.

DEPARTMENT OF CHEMISTRY
DE PAUL UNIVERSITY
CHICAGO, ILLINOIS

RECEIVED AUGUST 16, 1933
PUBLISHED OCTOBER 6, 1933

COMMUNICATIONS TO THE EDITOR

THE FREE METHYLENE RADICAL

Sir:

We have been decomposing diazomethane in a current of ether since some time, in attempts to isolate the methylene radical. Blank runs showed that ether alone, under the conditions of our experiments, does not decompose appreciably under 750°. Using the ether–diazomethane mixture and combining the fragments with metallic mercury [see Rice, Johnston and Evering, THIS JOURNAL, 54, 3529 (1932)] we obtained no trace of any organic compound of mercury with the furnace below 650°, although a considerable portion of the diazomethane decomposed, and antimony mirrors could be readily removed at furnace temperatures as low as 450°. A run at 700° gave an appreciable yield of an organo-mercury compound which was identified as dimethylmercury by adding iodine to the contents of the liquid air trap after distilling off the undecomposed diazomethane; in this way we obtained pure methylmercuric iodide, CH_3HgI, identified by its mixed melting point.

It seems reasonable to infer from these experiments that, if the CH_2 group has been formed, it does not combine with mercury to form $Hg=CH_2$, since the addition of iodine to this compound should give CH_2IHgI. Furthermore, it seems very probable that at temperatures of 700° and higher, the methylene group picks off a hydrogen atom from one of the surrounding ether molecules, thus producing a free methyl group.

In a further study of this problem we passed the ether-diazomethane mixture through a furnace heated only to 500°, under which conditions we had previously proved that no methyl groups are produced—and tried the effect of the fragments on metallic mirrors. We found that some metals were attacked and others not. Antimony and tellurium are two typical members of the first group, while zinc, cadmium and lead belong to the second group.

It seems possible to identify the fragments by combining them with tellurium and isolating the compound formed, or by combining them with carbon monoxide, in which case ketene, $CH_2{=}CO$, should be formed if we are dealing with a methylene radical. These experiments are now in progress.

JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
F. O. RICE
A. L. GLASEBROOK

RECEIVED AUGUST 29, 1933 PUBLISHED OCTOBER 6, 1933

AN APPARATUS FOR THE SEPARATION OF ISOHYDROGEN (DEUTERIUM) OXIDE BY ELECTROLYSIS

Sir:

The writers have not been able to find in the literature any description of an apparatus suited for the moderate scale production of heavy water (isohydrogen or deuterium oxide) by the method discovered by Washburn, that is, the electrolysis of water. An apparatus used in this Laboratory has proved so convenient for this purpose that some of its details may be of sufficient value to be presented.

Two concentric tubes of nickel, 2.5 and 10.6 cm. in diameter (Fig. 1) are used both as the electrodes and the vessel in which the aqueous solution is contained. The portion IJ, 100 cm. in height, holds 3.5 liters of the alkaline solution, supplied by the Burdette Oxygen Company. About 1 part in 2000 of the hydrogen present in this solution initially is deuterium.

The two tubes are insulated from each other by heavy rubber washers, H, Q and K. The washer K is cemented to the metal on which it rests. The screws which hold the apparatus together are insulated on one side by the Bakelite insulators D. The solution is put in or taken out at R, and a condenser and apparatus for the prevention of the escape of mist are attached at B. Electrical connections are made at A and E. The 2.5-cm. tube P is filled with water for cooling which is admitted at M. With 100 amperes operating current the water which escapes from N has a temperature only 0.3° above that which enters at M. The apparatus is made gas tight, except for the opening into the condenser, by the packing C.

The upper length of 10-cm. tubing, 15 cm. in length, is covered with rubber (F) from the inner tube of an automobile tire, and most of the wall of the steel tube is cut away. The purpose of the rubber is to avoid danger in any accidental explosion of the gas. The lower tube IJ is supposed to be kept as full of solution as is possible under the conditions of operation. The joint at H is not essential, as the upper part of the outer tube IJ may be cut away instead. One apparatus was built in which the upper tube was made wholly of rubber, and the connection between each D and H was made by an insulating post.

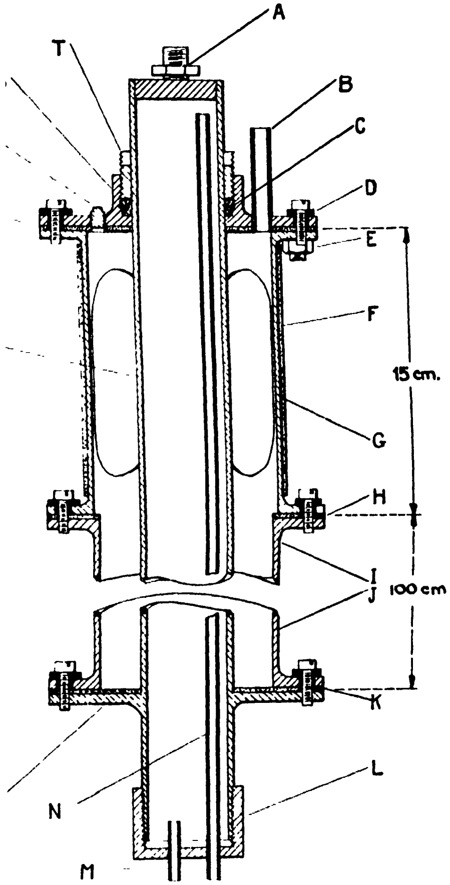

Fig. 1.—Apparatus for the separation of deuterium oxide.

The apparatus was designed to operate at 400 amperes, but this large a current has not been available.

To save expense the outer tube of our apparatus was made of steel, nickel plated on the inside, and this tube is therefore used as the electrode at which the hydrogen is liberated. The use of steel or iron for the inner tube is not recommended unless a very thick and dense nickel coating can be obtained.

Ten units such as that described are used for the preliminary separation. It is obvious that smaller units must be employed as the separation proceeds. The solution from one unit is distributed among the other nine as soon as space in them becomes available. It is planned to operate a second set of units of a different type, with acid solutions, and to use mutual neutralization as an aid to the separation of the water from the electrolyte.

In April, Dr. Washburn stated to one of us (Harkins) that he had tried the use of concentric tubes for the electrolysis, but we have no other knowledge of the apparatus employed by him.

UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

WILLIAM D. HARKINS
CLINTON DOBDE

RECEIVED SEPTEMBER 7, 1933 PUBLISHED OCTOBER 6, 1933

A POSSIBLE PHYSIOLOGICAL EFFECT OF THE HEAVY ISOTOPE OF H IN WATER

Sir:

While running experiments on the biological effect of melted ice water and recently condensed water [*Proc. Nat. Acad. Sci.*, **18**, 136, 422 (1932); **19**, 638 (1933)] I tried heavy water obtained from electrolysis in the manufacture of oxygen. The preliminary results are of interest in connection with the recent communication of G. N. Lewis [THIS JOURNAL, **55**, 3503 (1933)] reporting that tobacco seeds failed to sprout in pure H^2H^2O and that growth was considerably inhibited in water in which one-half of the hydrogen was H^2. Since the pure H^2H^2O appears to be lethal, it is probable that more interesting effects will be obtained with less concentrated water such as the sample used in the present experiments which had a specific gravity of 1.000061 (kindly determined by Drs. E. Ball and O. W. Richards).

The tests were made during May and June, 1933. In experiment No. 1 ten 250-cc. covered Pyrex beakers were used, each containing 90 cc. of water. There were four beakers of heavy water and two of each of the following: distilled water, melted ice water renewed daily, and freshly condensed water also renewed daily. Approximately equal amounts of freshly collected *Spirogyra* were rinsed in the water to be tested, drained on filter paper and placed in the beakers. The heavy water was changed after twenty-four hours to avoid dilution by water carried over with the filaments. The beakers were exposed to northern light in an unheated aquarium room (temp. 18–22°). Measurements with an illuminometer showed no differences in light intensity that might affect the results. The filaments in heavy water were characterized by their lack of movement, absence of abscission or cell disjunction [*cf.* Lloyd, *Mich. Acad.*, **6**, 275 (1927)] and greater longevity. In the distilled water controls more spreading occurred, the filaments broke into short lengths (abscission) and began to fade within twenty days. The usual effect was found in the ice and steam water, *i. e.*, almost normal condition in the former and bleaching in the latter. In experiment No. 2 consisting of two beakers of each of the four kinds of water the samples were buffered with Sørensen's phosphates to PH 7.16 and the effects secured again. In the third series the heavy water used in the preceding tests was redistilled in permanganate, buffered again and the results duplicated.

The experiments suggest a stabilizing action of water containing the heavy isotope and the hypothesis may be considered that this is an effect on the colloids in the organism whose bound water is known to be of greater density than "free" water.

PH determinations with brom thymol blue indicated a slightly higher *PH* for the heavy water. Further work with a glass electrode is planned to determine if this is a real effect, possibly due to the lower mobility of the heavy H isotope [*cf.* Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933)].

OSBORN ZOÖLOGICAL LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT
T. CUNLIFFE BARNES

RECEIVED SEPTEMBER 14, 1933 PUBLISHED OCTOBER 6, 1933

SCALE READINGS OF ISOMERIC ESTERS ON THE MAGNETO-OPTIC APPARATUS

Sir:

In a former report [THIS JOURNAL, **55**, 2614 (1933)] the scale readings of the characteristic minima of a number of organic compounds were determined and were found to increase with the increasing weight of positive radicals and to decrease with the increasing weight of the negative radicals. We desired to determine whether these observations held true in the case of isomeric esters or whether it might be that compounds having the same total mass would also have identical scale readings. In order to test this point, the scale readings of various types of esters which are isomeric with the normal alkyl acetates (published in the above mentioned report and reproduced here) were determined experimentally. The readings referred to carbon bisulfide are given in the table herewith.

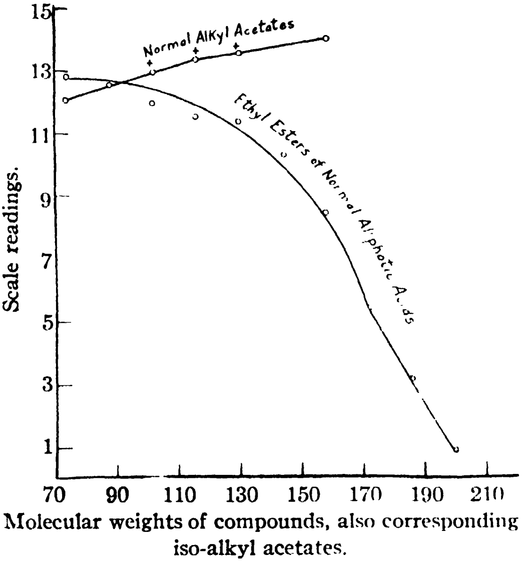

Fig. 1.—Scale readings of isomeric esters on the magneto-optic apparatus.

The usual precautions regarding impurities and contaminations were observed. All readings were made in both water and ether.

A study of the table will show that in the case of corresponding iso and normal acetates, where there is no change in the weights of the positive and negative radicals, the scale readings are identical. But for isomers such as methyl acetate and ethyl formate, where there is a change in the weight of both positive and negative radicals, different scale readings for the two compounds are obtained.

Ester	Scale Reading	Mol. Wt.	Ester	Scale Reading
Methyl acetate	12.00	74	Ethyl formate	12.74
Ethyl acetate	12.50	88	Ethyl acetate	12.50
Propyl acetate	12.97	102	Ethyl propionate	11.93
Butyl acetate	13.39	116	Ethyl butyrate	11.54
Amyl acetate	13.60	130	Ethyl valerate	11.42
		144	Ethyl caproate	10.32
Heptyl acetate	14.11	158	Ethyl heptylate	8.50
		172	Ethyl caprylate	5.50
		186	Ethyl pelargonate	3.26
		200	Ethyl caprate	0.89
Isopropyl acetate	12.97	102		
Isobutyl acetate	13.39	116		
Isoamyl acetate	13.60	130		

EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA
J. L. MCGHEE
MARGARET LAWRENZ

RECEIVED SEPTEMBER 16, 1933 PUBLISHED OCTOBER 6, 1933

THE SOLUBILITY OF SALTS IN H^2H^2O

Sir:

Preliminary experiments in this Laboratory have indicated that the solubility of salts in water containing a high concentration of H^2H^2O is markedly less than in ordinary distilled water at the same temperature. These solubility measurements were conducted in the usual way by preparing a saturated salt solution, removing and weighing a portion of the saturated solution, and finally weighing the residual salt after evaporation and suitable drying. By reason of the small volume of heavy water available, however, these operations were performed on a small scale using a special technique. The validity of the procedure was tested by first determining the solubility of a typical salt in ordinary water, and it was found that such solubility measurements could be made with an error of less than one per cent.

In the case of sodium chloride where 1.000 g. of ordinary water dissolves 0.359 g. at 25°, it was found that 1.000 g. of water containing 92% H^2H^2O dissolves only 0.305 g. of this salt, a difference of −15.0%. On a molar basis this corresponds to 0.111 mole of sodium chloride dissolved by a mole of ordinary water as contrasted to approximately 0.103 mole dissolved by one mole of heavy water, a difference of −7.2%. Similarly with barium chloride where 1.000 g. of ordinary water dissolves 0.357 g. of the anhydrous salt at 20°, it was found that 1.000 g. of water containing 92% H^2H^2O dissolves only 0.289 g. of the dehydrated salt at this temperature, a difference of −19.0%. This corresponds to 0.0309 mole of barium chloride dissolved by a mole of ordinary water in contrast to approximately 0.0275 mole dissolved by one mole of the heavy water, a difference of −11.0%. In the course of the last experiment well crystallized barium chloride hydrated with H^2H^2O was obtained with the view to examination for possible differences in crystal form as compared with the ordinary hydrate.

This decreased solubility of salts in H^2H^2O as contrasted with ordinary water is probably a general effect governed by the fundamental differences between the two liquids. Further investigation should show other interesting differences between the two liquids as solvents.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
HUGH S. TAYLOR
EARLE R. CALEY
HENRY EYRING

RECEIVED SEPTEMBER 19, 1933 PUBLISHED OCTOBER 6, 1933

SOME PROPERTIES OF HEAVY WATER

Sir:

We have measured a few characteristic properties of water containing various proportions of the heavy hydrogen isotope up to 92%, and have used these values for the purpose of extrapolation to 100%. The heavy water used in the experiments described in this communication was prepared by prolonged electrolysis of an alkaline solution with nickel electrodes. In estimating the proportion of H^2 from the density measurements, the value d^4_{20} 1.1056 given by Lewis and Macdonald [THIS JOURNAL, **55**, 3057 (1933)] was used. All our experimental data are given so that even should the figure 1.1056 later prove to be wrong, our results will not be without value. The molar quantities are calculated assuming the molecular weight to be 20.032.

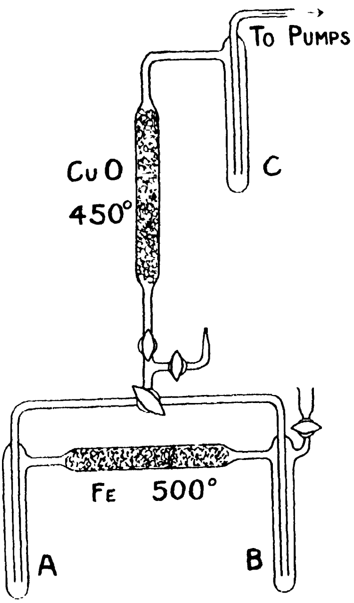

Fig. 1.—Apparatus for analysis of heavy water.

We have also attempted to determine the concentration of oxygen isotope O^{18} by decomposing the heavy water and combining the hydrogen and oxygen with ordinary oxygen and hydrogen, respectively. This was done in the apparatus shown. The heavy water was passed back and forth over hot iron between the traps A and B, liquid air being used to collect the fractions. As the hydrogen was released it was passed over hot copper oxide and the resulting water was caught in trap C (Fraction X). Ordinary dry, oxygen-

TABULATED DATA ON HEAVY WATER

	Ordinary water	31%	63.5%	92%	100% (calcd.)
Density d_{20}^{4}	0.9982	1.0314	1.0664	1.0970	1.1056 (Lewis)
Refractive index n_{20}^{D}	1.33293	1.33138	1.32992	1.32849	1.3281
Refractive index n_{20}^{C}	1.33094	1.32959	1.32824	1.32683	1.3265
Molar refr. (D line)	3.711	.....	.....	.....	3.677
Viscosity η_{20} (mp.)	10.87	11.4	12.7	13.7	14.2
Surface tension 20° (dynes/cm.)	72.75	71.5	69.8	68.1	67.8
Magnetic susceptibility $\chi \times 10^6$/g.	−0.72	.....	.....	−0.65	.....
Molar susceptibility × 10^6	−13	.....	.....	−13	.....

free hydrogen was passed over the iron-iron oxide mixture and the water formed was frozen out in A (Fraction Y). Excess hydrogen was burned at the jet shown.

Fraction X was found to be identical in properties with the initial heavy water. Fraction Y could not be distinguished from ordinary water. There is, therefore, no appreciable concentration of O^{18} in the electrolytic process.

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RECEIVED SEPTEMBER 22, 1933 PUBLISHED OCTOBER 6, 1933

NEW BOOKS

Ternäre Systeme. Elementare Einführung in die Theorie der Dreistofflegierungen. (**Ternary Systems.** An Elementary Introduction to the Theory of Three-Component Alloys.) By DR. G. MASING, Scientific Consultant, Siemens-Konzern, and Lecturer at the Technical High School of Berlin. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany, 1933. viii + 164 pp. 166 figs. 15 × 5 × 23.5 cm. Price, M. 8.30; cardboard cover, M. 9.60.

"The purpose of this work," writes the author, "is . . . to give the fundamentals of the science of ternary systems in complete representation," somewhat freely translated. This has been done to a fuller extent than in any other text, as far as the reviewer knows. Even the standard Roozeboom, in the latest section on three-component bodies, issued as long ago as 1913, omits discussion of the occurrence of solid solutions, which a practical metallurgist could hardly leave out of consideration. Masing's text is particularly complete with respect to the treatment of systems in which solid solution occurs, and is written with thoroughness and clarity. The first eight chapters contain discussion of a purely general nature, on isotherms, crystallization processes and representations of isoplethal sections ("zur Konzentrationsebene sehnrechte Schnitte"). This purely general treatment is intentional, and advantageous to the author's plan of making the treatment complete; an occasional reference to actual systems which show the peculiarities under discussion might make the book easier reading. The final three chapters discuss the iron–silicon–aluminum alloys, the tin–zinc alloys and the iron–carbon system. The book will be valuable to anyone desiring a more complete understanding of ternary systems than is at present to be had from the text-books previously available.

ARTHUR E. HILL

Grundlagen der Photochemie. (Fundamentals of Photochemistry.) By DR. K. F. BONHOEFFER and DR. P. HARTECK. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1933. viii + 295 pp. 73 figs. 15 × 22.5 cm. Price, RM. 24; bound, RM. 25.

A series of monographs on chemical reactions, mainly from a physico-chemical standpoint, is auspiciously begun by the present volume. It is promised that problems related to physics and biochemistry, and practical applications, will not be neglected.

The authors are not here concerned with photochemical apparatus or experimental details. Rather, they aim to present the theoretical principles which appear well established as a basis for the explanation of photochemical reactions. Hitherto, the chemist has been obliged to acquire these mainly from the writings of physicists. and to exercise no little critical judgment in so doing.

The first part of the book deals with general theories regarding the excitation of atoms and molecules due to the absorption of light quanta. The second part applies these in detail to the photochemical reactions of greatest interest at the present time. The last part deals with the interpretation of quantum yields and the kinetics of secondary reactions.

In almost all instances, a thorough knowledge of the literature is shown and the discussion of controversial points is in a high degree open minded and intelligent. It should be noted, however, that the quantum yield in the photolysis of uranyl oxalate is not unity, but varies between 0.4 and 0.6 according to the wave length of light absorbed. Also, the secondary reaction involved can scarcely depend upon collisions of excited uranyl ions with oxalate ions, as contended by the authors, unless a chain reaction involving fifty or more members occurs. This follows necessarily from the feeble dissociation of uranyl oxalate and the relatively small extinction coefficient of free uranyl ion.

A thorough study of this excellent book will lead to higher standards in the planning and interpretation of photochemical research.

GEORGE S. FORBES

Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. XIII. By DR. W. H. CAROTHERS, Editor-in-Chief, L. F. FIESER, R. C. FUSON, JOHN R. JOHNSON, C. R. NOLLER and W. W. HARTMAN. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1933. vii + 119 pp. 15.5 × 23.5 cm. Price, $1.75.

The editors of "Organic Syntheses" have devised a means of endowing their publication with perpetual youth: After increasing their number from year to year, they now retire to the honorable position of an "advisory board" and leave the active work to a new editorial board composed entirely of younger men. In the present volume the new board has demonstrated its quality by securing the collaboration of an uncommonly large number of contributors and by presenting the following unusually interesting variety of preparations: Allantoin; Azelaic Acid; 2-Phenyl-4-(3′,4′-dimethoxybenzal)-oxazolone; Benzalphthalide; β-Benzoylpropionic Acid; *n*-Butyl Borate; *iso*-Butyl Bromide; Butyroin; *m*-Chlorobenzaldehyde; 1,4-Dibenzoylbutane; 2,4-Dinitrophenylhydrazine; Diphenyl Triketone; Ethoxyacetic Acid and Ethyl Ethoxyacetate; Fluorobenzene; *p*-Fluorobenzoic Acid; Methoxyacetonitrile; Methyl Iodide; α-Methyl-α-phenylhydrazine; Methyl *iso*-Propyl Ketone; 1-Nitro-2-acetylaminonaphthalene; 2-Nitrofluorene and 2-Aminofluorene; 1-Nitro-2-naphthol; *N*-Nitrosomethylaniline; Nitrosomethylurethane; Perbenzoic Acid; *o*-Propiophenol and *p*-Propiophenol; *o*-Toluamide; *sym*-Tribromobenzene; Tricarbomethoxymethane; Veratric Aldehyde.

E. P. KOHLER

BOOKS RECEIVED

August 15, 1933–September 15, 1933

EMIL ABDERHALDEN. "Methodik des Nachweises von Abwehrfermentwirkungen." Handbuch der biologischen Arbeitsmethoden. Abt. IV, Angewandte chemische und physikalische Methoden, Teil 1, Heft 8. Urban und Schwarzenberg, Friedrichstrasse 105B, Berlin N 24, Germany. 70 pp. RM. 3.50.

K. FREUDENBERG. "Tannin, Cellulose, Lignin." Zugleich zweite Auflage der "Chemie der natürlichen Gerbstoffe." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 165 pp. RM. 8.80.

PHILIP LENARD. "Great Men of Science. A History of Scientific Progress." Translated from the German by H. Stafford Hatfield. The Macmillan Company, 60 Fifth Ave., New York. 389 pp. $3.00.

KARL MYRBÄCK AND HANS V. EULER. "Das Co-Enzym der alkoholischen Gärung, die Co-Zymase, ihr eBestimmung und Isolierung." TORSTEN THUNBERG. "Eine enzymatisch-chemische Methode zur Bestimmung von Zitronensäure." RUDOLF WEIDENHAGEN. "Karbohydrasen." Abderhalden, Handbuch der biologischen Arbeitsmethoden. Abt. IV, Angewandte chemische und physikalische Methoden, Teil 1, Heft 7. Urban und Schwarzenberg, Friedrichstrasse 105B, Berlin N 24, Germany. 88 pp. RM. 4.

E. H. RIESENFELD. "A Manual of Practical Inorganic Chemistry, Qualitative Analysis and Inorganic Preparations." Translated by P. Rây. Chuckervertty, Chatterjee, and Co., Ltd., 15 College Square, Calcutta, India. 471 pp. Price, Indian, Rs. 6/-; foreign, 9s.

REINHARD SEKA. "Alkaloide." Abderhalden, Handbuch der biologischen Arbeitsmethoden, Abt. I, Chemische Methoden, Teil 11, Heft 6 (Nachtrag zu Abt. I, Teil 9). Urban und Schwarzenberg, Friedrichstrasse 105B, Berlin N 24, Germany. 356 pp. RM. 19.

NEVIL VINCENT SIDGWICK. "Some Physical Properties of the Covalent Link in Chemistry." The George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University. Cornell University Press, 124 Roberts Place, Ithaca, New York. 249 pp. $2.00.

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VOLUME 55 NOVEMBER, 1933 NUMBER 11

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT LABORATORIES, SOCONY-VACUUM CORPORATION]

The Vapor Pressures of Propane and Propylene

BY ALFRED W. FRANCIS AND GEOFFREY W. ROBBINS

The vapor pressure of propane has been determined in five investigations,[1] but no two of them which cover the same temperature range agree with each other within about 5% in the value of the pressure (Fig. 2). The most recent investigation[1b] would seem the most reliable, judging by the care in purifying the samples and the consistency of results; but it gives a boiling point of −42.2°, which is about two degrees higher than any other reported in the literature for this hydrocarbon (except one, −37°,[1c] which is certainly too high). The vapor pressures are correspondingly at least 6% less than any other recorded values.

Three publications on the vapor pressure of propylene[1a,d,2] are more consistent, although no two cover the same temperature range.

In a recent investigation in this Laboratory an accuracy of about 1% was required in the vapor pressures of both these hydrocarbons at ordinary temperatures. Therefore, it seemed best to redetermine them. An all-glass apparatus simple both to construct and to operate was devised for this purpose. The elaborate apparatus and technique which would be required for a higher accuracy were not justified by the importance of this phase of the problem; but, since the results show less spread than those of any previous investigation, they seem worthy of record, together with a graphical comparison of all the published data.

Preparation of Materials.—Propane obtained by purchase was purified by fractional distillation at atmospheric pressure in a Davis column.[3] The finished sample distilled constantly within 0.1° at −42.3° (corr.). None of it was absorbed by sulfuric acid in a gas analysis pipet, indicating no propylene.

Propylene was made by catalytic decomposition of pure isopropanol in a bomb. It distilled constantly between −47.5 and −47.4° (corr.). In sulfuric acid it dissolved completely except for a tiny bubble, probably air from the connecting tube, which was too small to be transferred from the buret to the absorption pipet.

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[1] (a) Burrell and Robertson, THIS JOURNAL, **37**, 2188 (1915); (b) Dana, Jenkins, Burdick and Timm, *Refrig. Eng.*, **12**, 387 (1926); (c) Hainlen, *Ann.*, **282**, 233 (1894); (d) Maass and Wright, THIS JOURNAL, **43**, 1098 (1921); (e) Olszewski, *Ber.*, **27**, 3305 (1894).

[2] Seibert and Burrell, THIS JOURNAL, **37**, 2683 (1915).

[3] Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

The pentane thermometer used in these distillations was standardized at the ice point and at −50° by comparison with a standardized German thermometer, and the stem correction was computed from a previous investigation involving shifting the position of the thermometer. Barometer corrections also were applied to the boiling point readings.

Apparatus.—The apparatus consisted of a glass tube shown in Fig. 1, with a manometer on one leg and the sample confined with mercury on the other leg.

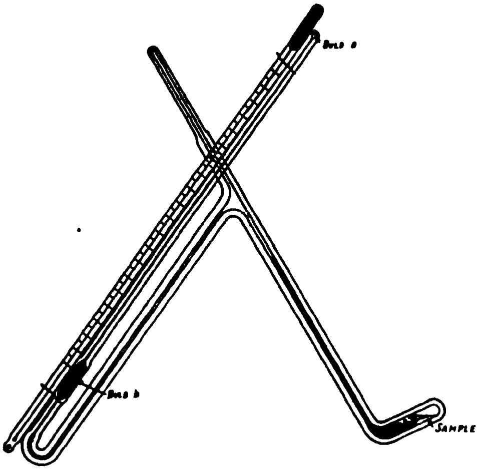

Fig. 1.—Absolute vapor pressure apparatus.

The manometer serves to measure the pressure by application of the gas laws to the air contained in it. Deviations from the gas laws at the temperatures and pressures studied are small (less than 0.35%)[4] but these corrections were applied in the calculations. The temperature and volume of that air must be measured accurately both with the apparatus open (and a known barometric pressure) and with the apparatus sealed and an otherwise unknown pressure. The temperature was measured by the attached thermometer. The manometer consists primarily of a fine uniform capillary tube, so that volume changes of its air content are proportional to length of air column as observed by the thread of confining mercury. But since the pressures to be measured are in the range 10 to 25 atmospheres, an accuracy in reading corresponding to that of a uniform tube over 120 cm. long is obtainable with one only 25 cm. long by substituting bulbs for the upper and lower portions.

Before constructing the apparatus the manometer was calibrated by weighing the tube with various parts filled with mercury. The capillary was thus found to have a cross section of 0.256 sq. mm. uniform within 1%. The small bulb (*a*) at the upper end has a capacity of about 0.006 ml., and the large bulb (*b*) about 0.25 ml.

The apparatus was exhausted several times and refilled with dry air through a calcium chloride tube so as to eliminate water vapor in the manometer, which would make the air too compressible and give high readings for the pressures. Mercury was then introduced by means of a capillary funnel, and the amount of air in the manometer adjusted by gentle suction until, when the manometer was held vertical, one mercury level was in the short portion of fine capillary below the bulb (*b*), while at the same time there was in the wide capillary connecting tube enough mercury (about 0.3 ml.) to fill the bulb (*b*) and fine capillary when it was driven there by pressure.

Operation.—The sample bulb was filled about 75% full with mercury, which was then heated to boiling to expel any adsorbed vapors. After cooling, the sample bulb was immersed with the filling tube in a vertical position in a cold bath of acetone and dry ice, causing the mercury to freeze. Pure propylene or propane was distilled through a calcium chloride drying tube and a capillary funnel into the sample bulb until the latter was filled completely with liquid sample on top of the frozen mercury. The end of the filling tube was sealed. The apparatus was withdrawn from the bath and held with the filling tube vertical until the mercury melted, when it was tipped to the position shown in the figure, confining the sample without a bubble. The sample bulb was then

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(4) "Int. Crit. Tables," McGraw-Hill Book Co., New York, 1928, Vol. III, p. 10.

immersed in a bath of water in a four-liter beaker by hanging the apparatus over the side of the beaker. The bath was agitated with an air stream and heated with a flame as warm as possible without allowing any of the sample to spill past the mercury into the capillary filling tube, and the flame shut off. A reading was taken every five or ten minutes during spontaneous cooling of the bath, as this gave very uniform temperatures, the rate of cooling being only about 0.1° per minute. The temperature of the sample was read in most cases on a short range (30–50°) thermometer divided into fifths of a degree, by immersing it in the bath near the sample bulb. This thermometer was calibrated with fused sodium sulfate giving a reading of 32.40°. The pressure was corrected for mercury heads in the connecting tube. The observations on vapor pressure are recorded in the table.

OBSERVED VAPOR PRESSURES

Temperatures in °C. Pressures in atmospheres

Propane				Propylene			
Filling 1		Filling 2		Filling 1		Filling 2	
t	*p*	*t*	*p*	*t*	*p*	*t*	*p*
31.9	11.8	27.6	10.4	29.0	12.8	30.2	13.3
36.0	13.0	29.6	11.1	31.4	13.5	32.3	13.9
38.2	13.6	32.0	11.7	32.3	13.9	35.2	14.9
42.0	15.0	34.1	12.4	34.2	14.7	39.1	16.4
42.2	15.2	34.9	12.5	34.3	14.7	42.2	17.5
44.5	15.8	35.4	12.7	35.9	15.1	44.0	18.2
45.6	16.0	36.5	13.1	36.0	15.2	45.1	18.7
47.5	16.9	37.2	13.3	37.3	15.6	45.8	18.8
49.8	17.7	38.5	13.7	39.3	16.3	Filling 3	
51.5	18.5	39.0	13.7	42.3	17.5	29.1	12.9
53.7	19.2	40.5	14.2			33.4	14.1
57.0	20.4	40.6	14.3			33.9	14.3
57.0	20.6	42.2	14.8			35.6	14.7
58.0	21.1	43.4	15.2			37.7	15.4
58.4	21.1	43.4	15.3			41.0	16.7
61.0	22.4	45.2	16.0			41.7	17.0
63.6	23.7	46.4	16.3			42.4	17.1

All the results of this investigation together with all published determinations of the vapor pressures of these two hydrocarbons (except those below −70° and one other) are plotted in Fig. 2. The abscissas are plotted as $1000/T$, but the lines indicate actual temperature centigrade. In order to decrease the slope of lines plotted and so permit a much larger scale, the ordinates are $(1000/T) + \log P$ instead of merely $\log P$, as is customary. A wavy line is drawn to separate the points for the two hydrocarbons, since the fields containing the points almost overlap.

Our own values do not cover a sufficient temperature range to determine the exact slope of the vapor pressure curves. It seems preferable to include the normal boiling points to determine the slope. Our observation on propane, −42.3°, agrees well with that of Dana, Jenkins, Burdick and Timm,[1b] −42.2°, and is much higher than three others in the literature, −44.1°,[1a] −44.5°[1d] and −45.0°.[1e] Our value for propylene, −47.5°, is nearly the mean of three recorded in the literature, −47.0°,[1d] −47.8°,[1a] and −47.6° (corr.).[3]

The best straight lines are drawn in the figure through the points corresponding to these boiling points and those for vapor pressures. They correspond to the equations for propane $\log P_1 = 4.375 - (1010/T)$ and for propylene $\log P_2 = 4.357 - (983/T)$.

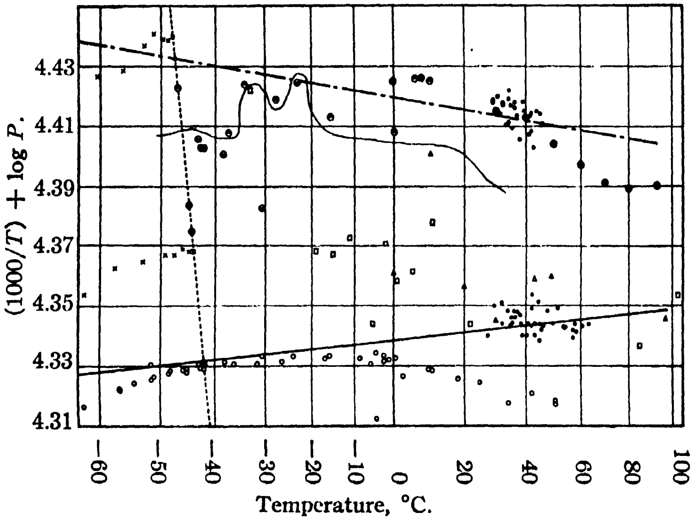

Fig. 2.—Vapor pressures of propane and propylene: propane———; propylene—— –; locus of normal boiling points– –; Burrell and Robertson, ×; Dana, Jenkins, Burdick and Timm, ⊙; Francis and Robbins, ●; Hainlen, □; Maass and Wright, propane, ⊖, propylene, ◓; Olszewski, △; Seibert and Burrell, ⊗.

The former line agrees within about 1% with most of the determinations of Dana, Jenkins, Burdick and Timm[1b] up to 0°, but their values for higher temperatures diverge considerably. A plot of their points gives a line of much greater curvature than would be expected for a non-polar substance like propane.

The straight line for propylene agrees as well as any other with the various determinations in the literature.

Summary

An all-glass apparatus was devised for determining vapor pressures above atmospheric.

The vapor pressures of propane and propylene have been determined in the same apparatus for the first time above 0°. The determinations cover a temperature range of 27 to 64° for propane and 29 to 46° for propylene.

PAULSBORO, NEW JERSEY

RECEIVED MARCH 8, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Partial and Integral Heats of Dilution of Cadmium Sulfate Solutions from Electromotive Force Measurements[1]

BY VICTOR K. LA MER AND W. GEORGE PARKS

Introduction

In a previous paper[2] we reported electromotive force measurements for 0 and 25° on the cell

$$\text{Cd (2 phase amalgam), } CdSO_4 \text{ (m), } PbSO_4 \text{ (s), Pb (2-phase amalgam)} \qquad (1)$$

for which the cell reaction is

$$\text{Cd (s, satd. with Hg)} + PbSO_4 \text{ (s)} = CdSO_4 \text{ (m)} + \text{Pb (s, satd. with Hg)} \qquad (2)$$

By comparing the observed values of the activity coefficient, f, of cadmium sulfate which may be obtained from these measurements with the predictions of the theory of Gronwall, La Mer and Sandved[3] we found that the Debye–Hückel parameter "a" assumed the constant and physically plausible value of 3.6 Å. for both temperatures. From these data we reported preliminary values for the *mean* heat of dilution of cadmium sulfate for 12.5°.

To verify the important conclusion that $\partial``a"/\partial T$ is zero and to determine more precisely and more accurately the true heat of dilution of cadmium sulfate by considering the partial heat capacity of this salt, we have reinvestigated this cell for ten-degree intervals extending from 0 to 30° in the region of high dilution with improved apparatus for low temperature control. The theoretical treatment will follow closely the form presented in a recent paper by La Mer and Cowperthwaite[4] for the analogous cell involving the formation of zinc sulfate, from which the heat capacities and heats of dilution of this salt have been reported. We shall also reconsider our previous measurements in the light of Wyman's[5] improved values for the temperature coefficients of the dielectric constant of water which appeared after the computations in the previous paper had been completed.

Experimental

The measuring instruments, purification of materials, analytical technique and the method of filling and handling the electrode vessel have been described in detail previously.[2] An 11% by weight cadmium amalgam was employed since it has been shown by Jaeger and Steinwehr[6] in an investigation of the Weston standard cell that a 12.5%

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[1] The experimental work of this paper was performed by W. George Parks in 1930–1931 while Lecturer in Chemistry in Columbia University. He is at present Assistant Professor of Chemistry in the Rhode Island State College.

[2] La Mer and Parks, THIS JOURNAL, **53**, 2040 (1931).

[3] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[4] La Mer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933).

[5] Wyman, *Phys. Rev.*, **35**, 623 (1930).

[6] Jaeger and Steinwehr, *Z. physik. Chem.*, **97**, 319 (1921).

amalgam showed no abnormal behavior on being cooled from 60 to 0°. Smith,[7] who studied amalgams containing from 1 to 20% cadmium, recommends a 10% amalgam as being stable between 51 and 0°. Vosburgh and Eppley[8] found the abnormally high electromotive force of standard cells after a decrease in temperature to be only temporary. Cohen and Kruyt[9] show a 10 and 12.5% amalgam to be normal at 0 and 25°.

A special thermostat which permits of rapid control of temperature was constructed of copper-lined Balsa wood. Cooling brine from a refrigerating unit operating at −15°. was circulated through copper coils at a rate depending upon the temperature desired. Alcohol was added to the bath liquid to prevent the formation of ice on the coils, which otherwise would interfere with precise temperature regulation. The temperature could be maintained to ±0.01° by thermostatic control with electric heaters. A special form of mercury regulator which facilitates rapid adjustment of temperature will be described in a separate note.[10] With this improved apparatus it was considered advisable to repeat the measurements previously made at 0°. In the earlier work 0° was obtained by an ice and water mush, and the temperature was lowered from 25 to 0° in one step. Lowering the temperature slowly by 10° intervals is believed to be a more reliable procedure.

A constant electromotive force was invariably obtained more rapidly by passing successively from higher to lower temperatures (twelve to eighteen hours) than by passing from lower to higher temperatures where approximately fifty hours were required. The saturation equilibrium for lead sulfate is attained more rapidly from supersaturation than from undersaturation, undoubtedly due to the slowness of the diffusion process in the latter case. In general the temperature level was established about 5 P. M. and the following day readings were made at intervals of an hour from 9 A. M. to 4 P. M. These values checked to within ±0.02 mv. Adjustment to a lower temperature level was then made and the procedure repeated. After the value at 0° had been established, measurements were made at ascending temperatures on the same cell over a three-day period at each temperature. Except in rare instances the second set of values checked the first within ±0.02 mv. The values of E, observed, recorded in Table I, represent the average of two cells. For $m = 0.02$ and $m = 0.002$ the average refers to three separate cells. The readings on different cells which are accepted checked each other within ±0.04 mv. The Leeds and Northrup type K potentiometer was calibrated by us in coöperation with Dr. MacInnes' staff at the Rockefeller Institute for Medical Research to the nearest 0.01 mv. We emphasize the importance of calibrating all potentiometers when using them for precision work. Two working standard cells, one immersed in a thermostat at 25° and the other in a room where the temperature always remained within the range of 22 to 27°, were employed. These cells were checked in this Laboratory and at the Rockefeller Institute at intervals against standard cells which had been certified recently by the Bureau of Standards.

Experimental Results

The method of correcting the experimental data given in Table I for the solubility of lead sulfate has been explained in detail in our first paper.[11] In Table II we give the numerical values of the coefficients in equation 4 [the Gronwall, La Mer and Sandved, eq. (107)] corrected to comply with Wyman's values for the dielectric constant of water, necessary for com-

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(7) Smith, *Phil. Mag.*, **19**, 250 (1910).

(8) Vosburgh and Eppley, THIS JOURNAL, **46**, 109 (1924).

(9) Cohen and Kruyt, *Z. physik. Chem.*, **65**, 359 (1909).

(10) W. G. Parks, *Ind. Eng. Chem., Anal. Ed.*, **5**, 357 (1933).

(11) La Mer and Parks, Ref. 2, p. 2049. (See Fig. 4.) The solubility data of Kohlrausch and Huybrechts and de Langeron are employed in our present calculations.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL Cd-Hg (2-PHASE), $CdSO_4$ (m), $PbSO_4$ (s), Pb-Hg (2-PHASE) AT 0, 10, 20, 30°. COMPUTATION OF $E^{\circ\prime}$ AND E°

Molality $CdSO_4$	$E_{(obs.)}$	$RT/n\mathbf{F}$ ln $SO_4^{=}$	$RT/n\mathbf{F}$ ln Cd^{++}	$E^{\circ\prime}$	$RT/n\mathbf{F}$ ln $f_{1,3,5}$ "a" = 3.6 A.	E°	Deviation from mean
Temperature, 0°C.							
0.0005	0.20042	-0.08882	-0.08944	0.02216	-0.00558	+0.01658	+0.00002
.001	.18692	- .08109	- .08129	.02456	- .00798	.01658	+ .00002
.002	.17388	- .07307	- .07313	.02768	- .01118	.01650	- .00006
.005	.15796	- .06233	- .06235	.03328	- .01667	.01661	+ .00005
.01	.14648	- .05419	- .05419	.03810	- .02156	.01654	- .00002
.02	.13497	- .04603	- .04603	.04291	- 02686	.01605	
					Mean =	+0.01656	
Temperature, 10°C.							
0.0005	0.20274	-0.09195	-0.09273	0.01806	-0.00589	+0.01217	+0.00005
.001	.18887	- .08403	- .08427	.02057	- .00843	.01214	+ .00002
.002	.17548	- .07574	- .07581	.02393	- .01182	.01211	- .00001
.005	.15896	- .06462	- .06464	.02970	- .01761	.01209	- .00003
.01	.14719	- .05617	- .05618	.03484	- .02273	.01211	- .00001
.02	.13547	- .04772	- .04772	.04003	- .02827	.01176	
					Mean =	+0.01212	
Temperature, 20°C.							
0.0005	0.20277	-0.09496	-0.09599	0.01182	-0.00624	+0.00558	+0.00003
.001	.18865	- .08691	- .08724	.01450	-0.00894	.00556	+ .00001
.002	.17491	- .07838	- .07849	.01804	- .01253	.00551	- .00004
.005	.15799	- .06689	- .06691	.02419	- .01863	.00556	+ .00001
.01	.14588	- .05815	- .05816	.02957	- .02401	.00556	+ .00001
.02	.13402	- .04941	- .04941	.03520	- .02979	.00541	
					Mean =	+0.00555	
Temperature, 30°C.							
0.0005	0.20168	-0.09808	-0.09928	0.00432	-0.00663	-0.00231	-0.00003
.001	.18724	- .08984	- .09023	.00717	- .00949	- .00232	- .00002
.002	.17313	- .08105	- .08117	.01091	- .01331	- .00240	+ .00006
.005	.15576	- .06917	- .06920	.01739	- .01976	- .00237	+ .00003
.01	.14341	- .06014	- .06015	.02312	- .02541	- .00229	- .00005
.02	.13152	- .05110	- .05110	.02932	- .03144	- .00212	
					Mean =	-0.00234	

puting the theoretical value of the activity coefficient given in column 6 of Table I. The quantities in Table I are defined by the equations

$$E_{(obs.)} = E^{\circ} - \frac{\nu}{n}\frac{RT}{\mathbf{F}}\ln m - \frac{\nu}{n}\frac{RT}{\mathbf{F}}\ln f = E^{\circ\prime} - \frac{\nu}{n}\frac{RT}{\mathbf{F}}\ln f \qquad (3)$$

$$\ln f = \frac{-\epsilon^2 z^2}{kTD_0 a}\,\frac{1}{2}\,\frac{x}{1+x} + \sum_{m=1}^{\infty}\left(\frac{\epsilon^2 z^2}{kTD_0 a}\right)^{2m+1}\left[\frac{1}{2}\ X_{(2m+1)}\ (x)_{-2m}\ \ Y_{2m+1}\ (x)\right]^{12} \qquad (4)$$

TABLE II

NUMERICAL VALUE OF THE COEFFICIENTS IN THE GRONWALL, LA MER AND SANDVED EQ. (107), CORRECTED FOR WYMAN'S VALUES FOR THE DIELECTRIC CONSTANT OF WATER

t, °C.	D_0	$\frac{1}{2.3026}\,\frac{\epsilon^2}{2kTD_0} \times 10^{8}$	$\frac{1}{2.3026}\left(\frac{\epsilon^2}{kTD_0}\right)^3 \times 10^{21}$	$\frac{1}{2.3026}\left(\frac{\epsilon^2}{kTD_0}\right)^5 \times 10^{36}$
0	88.00	1.50093	0.143418	0.068520
10	84.12	1.51469	.147400	.071720
20	80.36	1.53147	.152352	.075781
30	76.75	1.55060	.158133	.080634

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(12) The numerical values of the universal constants are consistent with those employed by La Mer and Cowperthwaite, THIS JOURNAL, 53, 4333 (1931), and Ref. 4.

The values for $E^{\circ\prime}$ for 0, 10, 20 and 30° are plotted as a function of $\sqrt{m}$ in Fig. 1. The straight lines represent the Debye–Hückel limiting law while the heavy lines correspond to the predictions of the extended theory for "a" = 3.60 Å. The deviations from the theoretical curve are not perceptible on this plot but their magnitude is represented by the deviations of the individually computed values for E° given in column 8 of Table I. Computations employing values of "a" equal to 3.64 and 3.56 Å. show that "a" = 3.60 Å. gives the best fit with the experimental data.

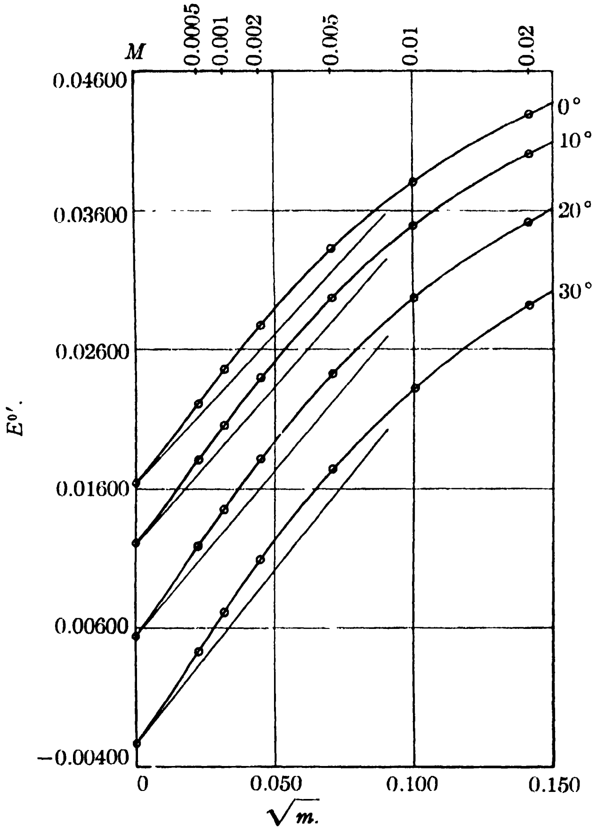

Fig. 1.

It will be noted that these deviations seldom exceed what might be attributed to experimental error at the temperature studied. It was our intention to extend our measurements to higher temperatures for a more extended test of the conclusion that ∂"a"$/\partial T$ is zero. Unfortunately, we find that at temperatures between 30 and 37° the electromotive force values become uncertain due undoubtedly to a transition in the solid cadmium.[13]

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[13] Cohen, "Physico-Chemical Metamorphosis and Problems in Piezochemistry," McGraw-Hill Book Co., Inc., New York, 1928, pp. 40–50; Getman, THIS JOURNAL, 39, 1806 (1917).

In our previous paper we found that "a" = 3.6 Å. gave the best fit for our data at 0 and 25° when Drude's value for D_0 is employed. The earlier data for 25° are recalculated in Table III using Wyman's value for D_0.

TABLE III

VALUES OF E_0 AT 25° "a" = 3.60 Å.

M	Drude D_0 = 78.77 Deviation from mean	Wyman D_0 = 78.54 Deviation from mean
0.0006070	−0.00010	−0.00005
.0007267	+ .00001	+ .00005
.0008675	− .00005	− .00002
.0009609	− .00004	± .00000
.0009819	− .00004	± .00000
.001077	− .00006	− .00003
.001119	+ .00001	+ .00004
.001332	− .00007	− .00004
.001993	− .00006	− .00004
.002994	− .00008	− .00008
0.003807	−0.00009	−0.00006
.004371	− .00003	− .00004
.005618	+ .00008	+ .00006
.007544	+ .00008	+ .00005
.007901	+ .00009	+ .00005
.008351	+ .00009	+ .00006
.009307	+ .00005	+ .00001
.009409	+ .00007	+ .00003
.01096	+ .00007	+ .00003

Mean (D) = +0.00142 ± 0.00006 (a. d.). Mean (W) = +0.00133 ± 0.00004 (a. d.)

When the results for $E^{\circ\prime}$ in column 5, Table I, are interpolated for 25° and compared with the previous work at 25° by interpolating graphically (Ref. 2, Fig. 5) to rounded molalities, we obtain the following differences between the two series for m = 0.000 to m = 0.02, namely: +0.06; −0.08; +0.01; −0.03; −0.02; +0.04; −0.07 mv. We consider this a satisfactory check on our work.

The best value of "a" is again 3.60 Å. Although the mean value of E° is reduced by 0.09 mv., it is gratifying to note that in this extensive series of measurements even better agreement with the extended theory is obtained by using Wyman's value instead of Drude's.

In Table IV we summarize the activity coefficients of cadmium sulfate calculated from the observed values of E and the mean value of E° given in Table I.

TABLE IV

THE ACTIVITY COEFFICIENTS OF $CdSO_4$

M	0°	10°	20°	30°
0.0005	0.788	0.784	0.780	0.775
.001	.712	.707	.702	.695
.002	.630	.616	.610	.602
.005	.491	.487	.478	.470
.01	.400	.394	.386	.377
.02	.326	.319	.309	.298

Heat of Dilution.—In Fig. 2 we plot the values of $E^{\circ\prime}$ given in Table I against the reciprocal of the absolute temperature. The slope of the curves at any point is a measure of the change in molal heat content, ΔH, of the cell process for the temperature and concentration of cadmium sulfate selected. Since the slopes change continuously it is evident that ΔH

varies considerably with temperature, which we shall show is due primarily to cadmium sulfate having a large negative value for its partial molal heat capacity. To detect changes in these quantities with changing concentration it is expedient to resort to numerical methods.

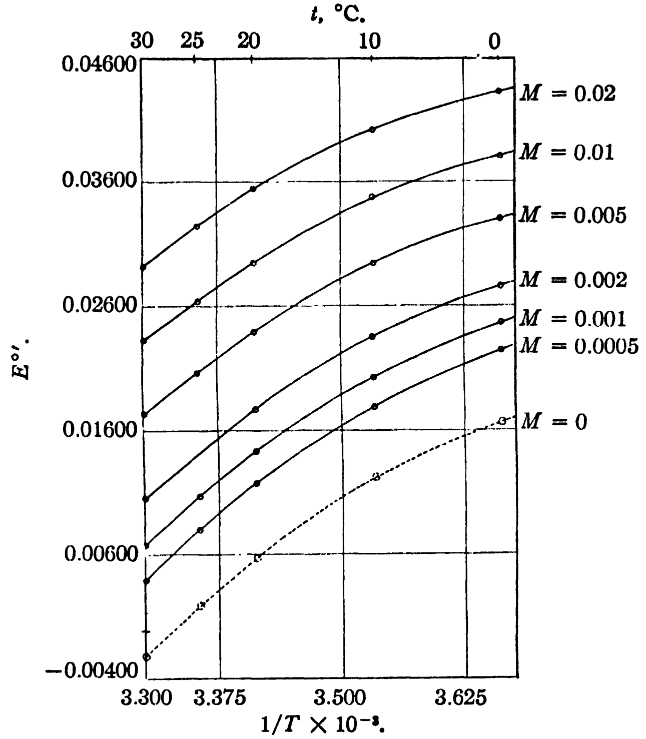

Fig. 2.

For purposes of computation La Mer and Cowperthwaite[4] showed that the Gibbs–Helmholtz equation assumes its most convenient form when written

$$-\Delta H = n\mathrm{F}[E^{\circ\prime} - T(\partial E^{\circ\prime}/\partial T)_P] \qquad (5)$$

By comparing the values for $-\Delta H$ at a finite concentration with the value for infinite dilution computed by setting $E^{\circ\prime} = E^{\circ}$, we can readily calculate $\bar{L}_2$, the partial molal heat of dilution of cadmium sulfate, by the equation

$$-\Delta H_{(m-0)} - (-\Delta H_{(m-m)}) = \bar{H}_2 - \bar{H}_2^0 = \bar{L}_2 \qquad (6)$$

corresponding to the process

$$\mathrm{CdSO_4}\,(m) = \mathrm{CdSO_4}\,(m = 0) + \bar{L}_2 \qquad (7)$$

In terms of the activity coefficient $\bar{L}_2$ can be written

$$\bar{L}_2 = -\nu RT^2\,(\partial \ln f/\partial T) \qquad (8)$$

Introducing the limiting law of the Debye–Hückel theory for $\ln f$, equation (8) takes the form

$$\overline{L}_2 = -{}^3/_4\,\frac{\nu R\epsilon^2 z^2}{kD_0}\,\kappa\left(1+\frac{T}{D_0}\frac{\partial D_0}{\partial T}+\frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T}\right)^{\text{[14]}} \tag{9}$$

Having obtained $\overline{L}_2$ with the aid of equation (6) the integral molal heat of dilution of cadmium sulfate, L, was computed (Table VIII) according to the formula $L = \frac{1}{m}\int_0^m \overline{L}_2 \mathrm{d}m$. The limiting law for L is

$$L = V_m = -N\sum_{j=1}^{s}\frac{\epsilon^2\nu_j z_j^2}{2D_0}\left[1+\frac{\partial \ln D_0}{\partial \ln T}+\frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T}\right]\kappa \tag{10}$$

When $\nu = 2$ the limiting slopes for $\overline{L}_2$ and L are given by the equations

$$\overline{L}_2/\sqrt{m})_{m\rightarrow 0} = -6N\epsilon^2\frac{1}{D_0}\left[1+\frac{\partial \ln D_0}{\partial \ln T}+\frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T}\right]\frac{\kappa}{\sqrt{m}} \tag{11}$$

$$L/\sqrt{m})_{m\rightarrow 0} = \frac{-4N\epsilon^2}{D_0}\left[1+\frac{\partial \ln D_0}{\partial \ln T}+\frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T}\right]\frac{\kappa}{\sqrt{m}} \tag{12}$$

In Table V we give a summary of the numerical values to be used in equations 9, 10, 11 and 12. The values for the limiting slopes are in calories mole^{-1} $m^{-1/2}$.

TABLE V

CALCULATION OF LIMITING SLOPE FOR $\overline{L}_2/\sqrt{m}$ AND $L/\sqrt{m}$

t, °C.	D_0	$\frac{\partial D_0}{\partial T}$	$\frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T}$	$\left[1+\frac{\partial \ln D_0}{\partial \ln T}+\frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T}\right]$	$\overline{L}_2/\sqrt{m}$	$L/\sqrt{m}$
10	84.12	−0.382	0.0012	−0.287	4410	2939
15	82.22	− .375	.0080	− .306	4830	3260
20	80.36	− .368	.0144	− .358	5789	3858

The change in heat capacity for the process, (2), can be calculated by the formula

$$\Delta C_p = nFT(\partial^2 E^{\circ\prime}/\partial T^2)_p \tag{13}$$

Computation of Thermal Quantities.—To reduce exaggeration of the experimental errors in the individual values of $E^{\circ\prime}$ in the differentiation process, we calculated values of $E^{\circ\prime}$ smoothed as a function of the concentration by the aid of equation 4. They differ from the experimental values by the amount given in the last column of Table I.

The smoothed values of $E^{\circ\prime}$ are then expressed as a polynomial of the third degree in terms of t°C., namely

$$E^{\circ\prime} = A + Bt + Ct^2 + Dt^3 \tag{14}$$

The values of the coefficients in Table VI, therefore, represent all of the smoothed values as a function of the temperature, from which it is an easy matter to compute $(\partial E^{\circ\prime}/\partial T)_p$ and $(\partial^2 E^{\circ\prime}/\partial T^2)_p$ for substitution in equations 5 and 13.

The results of these calculations are given in Table VII for the temperatures 10, 15 and 20°, where the values of the derivatives will be most reliable.

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(14) See La Mer and Cowperthwaite, Ref. 4, page 1006, for the definition and the numerical values of the fundamental constants employed; also for the derivation of the equations of this section.

TABLE VI

NUMERICAL VALUE OF COEFFICIENTS × 10^6 FOR EQUATION 14

m	A	B	C	D
0.0000	1656	−31.0500	−1.470	0.013500
.0005	2214	−27.9500	−1.480	.014500
.001	2454	−26.7833	−1.450	.013833
.002	2774	−25.4000	−1.375	.011500
.005	3323	−22.1500	−1.415	.013000
01	3810	−19.7833	−1.420	.013833
.02	4291	−16 0500	−1.425	.015000

TABLE VII

SUMMARY OF HEAT CALCULATIONS

m	ΔC_p	$-\Delta H$(process)	$\bar{L}_2$
	10°		
0.0000	−278	7929	
.0005	−273	7782	147
.001	−270	7695	234
.002	−269	7566	363
.005	−268	7454	475
.01	−263	7361	568
.02	−255	7080	849
	15°		
0.0000	−229	9198	
.0005	−219	9016	182
.001	−219	8922	276
0.002	−227	8809	389
.005	−219	8676	522
.01	−212	8548	650
.02	−199	8217	981
	20°		
0.0000	−179	10,219	
.0005	−165	9980	239
.001	−168	9892	327
.002	−185	9843	376
.005	−172	9658	561
.01	−160	9479	740
.02	−142	9071	1148

The values of $\bar{L}_2$ and L for 15° are plotted against $\sqrt{m}$ in Fig. 3. The light lines correspond to the theoretical limiting slopes computed in Table V.

The concentration dependence of $\bar{L}$ and L has the characteristic form predicted by the theory of Gronwall, La Mer and Sandved up to 0.01 M. The more rapid increase of $\bar{L}$ above 0.01 M is in agreement with our previous data for 0 and 25° (Ref. 2, Fig. 8). A similar type of curve has been observed for hydrochloric acid by Rossini and by Harned and Ehlers.[15]

It is important to emphasize that aside from using the extended theory as the most legitimate means available for extrapolating for E° and for the very minor influence of smoothing the experimental data, a correction which is comparable in magnitude to the experimental error, the numerical values of L and $\bar{L}$ are the result of purely thermodynamic operations upon the experimental data and do not depend upon this theory. If desired, any influence which the extrapolation for E° may exert upon these quantities can be eliminated completely by taking the reference state as m = 0.0005 instead of infinite dilution.

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(15) Rossini, *Bur. Standards J. Research*, **9**, 499 (1933); Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

In Fig. 4 we plot the values of $E^{0\prime}_{(m)} - E^{0\prime}_{(m=0.0005)}$ for the smoothed values and the corresponding smoothed values for zinc sulfate (Ref. 4, Table I) in order to compare the excess free energies of these two salts as a function of temperature. The differences are within experimental error at 0.001 and 0.002 molal but are of the order of 0.2 mv. at 0.01 molal, as would be expected since the "*a*" values differ perceptibly.

In Table VIII we give values of the integral heats of dilution for cadmium sulfate and zinc sulfate at 15°. These values were obtained by graphical integration using the formula $L = 1/m \int_0^m \bar{L}_2 dm$, and are in agreement with the values of the integral heat capacity difference per mole $(C_p - C_p^\circ)$ for zinc sulfate at 25° obtained by a similar integration of the $(\bar{C}_p - \bar{C}_p^\circ)$ values.

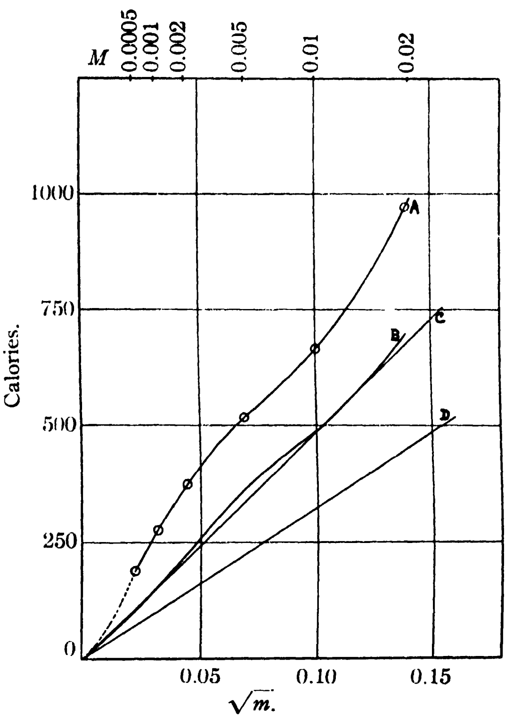

Fig. 3.—A = $\bar{L}_2$ ($CdSO_4$, 15°); B = L ($CdSO_4$, 15°); C = D.H.L.L. for $\bar{L}_2$ 15°; D = D.H.L.L. for L 15°.

Unfortunately the e. m. f. measurements for cadmium sulfate could not be extended over as large a temperature range as in the case of zinc sulfate. The values of $(\bar{C}_p - \bar{C}_p^\circ)$ which could be computed from Table VII are consequently not sufficiently consistent to justify the calculation of heat capacity quantities for cadmium sulfate as a function of concentration. The values of L at 15° are larger for cadmium sulfate than for zinc sulfate in qualitative agreement with the recent calorimetric measurements of Plake.[16]

TABLE VIII

MOLAL INTEGRAL HEATS OF DILUTION OF CADMIUM SULFATE AND ZINC SULFATE AT 15°

m..........	0.0005	0.001	0.002	0.005	0.01	0.02
$CdSO_4$ (15°)	99	158	249	378	483	642
$ZnSO_4$ (15°)	96	146	213	315	390	...
$ZnSO_4$ (25°)	157	246	366	571	739	...
$(C_p - C_p^\circ)$ $ZnSO_4$ (25°)	−5.8	−9.8	−15.2	−25.6	−35.1	...

We are indebted to Dr. I. A. Cowperthwaite for checking the graphical integrations

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[16] Plake, *Z. physik. Chem.*, **A162**, 257 (1932), p. 262.

The table illustrates how sensitive heats of dilution are to temperature and emphasizes the importance of comparing calorimetric measurements at a uniform temperature.

We do not claim that our computations of L and $\bar{L}$ are more accurate than those which can be obtained by the direct calorimetric methods now available. On the other hand, we are convinced that the values of "a" and of (∂"a"/∂T) which can be computed from free energy measurements at different temperatures are superior in reliability to those values which can be calculated from calorimetric data by the use of the Lange–Meixner equation, even though the data are of high accuracy.

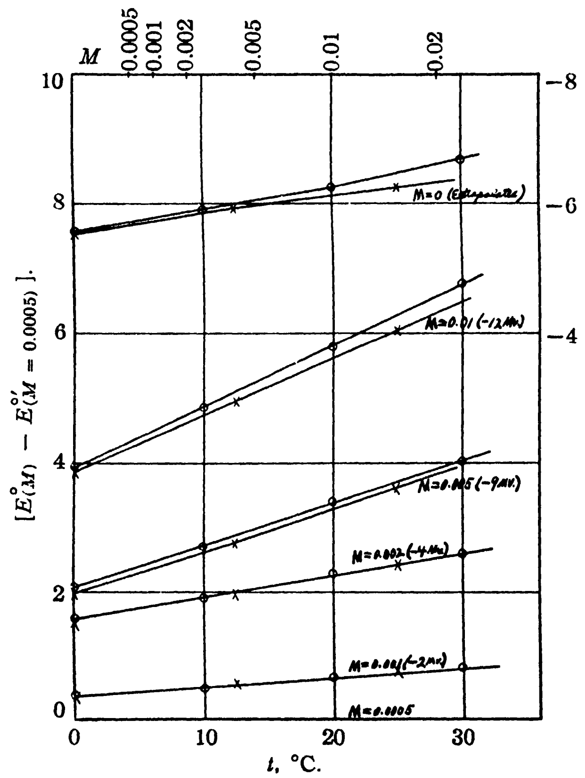

Fig. 4.—O, cadmium sulfate; X, zinc sulfate.

In 1930–1931 Dr. I. A. Cowperthwaite and one of us, with the assistance of the late Dr. T. H. Gronwall, computed numerical tables of the first and second derivatives of the X_3 and X_5 functions which are required for computing $\bar{L}$ and ($\bar{C}_p - \bar{C}_p{}^{\circ}$) by the extended theory. Our object was to compare the theoretical predictions of the extended theory using values of "a" established from free energy measurements with the directly measured values of $\bar{L}$ and ($\bar{C}_p - \bar{C}_p{}^{\circ}$). This procedure would test whether or not the values of $(\partial D/\partial T)$ and $(\partial^2 D/\partial T^2)$ determined on pure water corresponded with those actually required by the experimental data at finite concentrations. Unfortunately we found that the contributions of the third and fifth approximations for $\overline{L}$ and $(\overline{C}_p - \overline{C}_p{}^\circ)$ in addition to being extremely sensitive to variations in "a" did not converge with sufficient rapidity for the range of "a" values given by the convergent equation 4 to be of any use for this purpose. In fact the very much simpler equation for the integral heat of dilution, L

$$L = -1196\,(Z^2/a)\,x/(1 + x) + 59.45\,(Z^2/a)^3\,(10^3X_3) + 29.64\,(Z^2/a)^5\,(10^5X_5) \quad (15)$$

valid for water at 25°,[17] which involves functions of the X type only, does not converge as rapidly for the same value of "a" as does equation 4 for log f which involves functions of the type $({}^1/_2X_{2m+1} - 2mY_{2m+1})$. Table IX shows clearly the relatively greater importance of the third and fifth approximations for L as compared to log f. The third approximation contributes about one-half as much to log f as to L, whereas the fifth approximation contributes only one-third to one-seventh as much. The use of values of $(``a"/Z^2)$ other than 1 Å. will affect the rapidity of convergence but will not alter the relative importance of the third and fifth approximations for $L$ and log $f$ for the same value of $(``a"/Z^2)$. Our objections to "a" calculations from calorimetric data are based not only on the poor convergence and neglect of terms in $\partial V/\partial T$ in the Lange–Meixner equation but particularly to the uncertainty in the values of $(\partial D_0/\partial T)$,[18] which determine the coefficients in equation 15. The error produced by substituting $D = D_0$ is probably not very great, but we have no evidence as yet that $(\partial D/\partial T) = (\partial D_0/\partial T)$ for different salts at finite concentrations.[19]

TABLE IX

COMPARISON OF THE RAPIDITY OF CONVERSION OF THE EXTENDED THEORY IN TERMS OF LOG f (EQUATION 4) AND IN TERMS OF L (EQUATION 15) FOR $``a"/Z^2 = 1$ Å.; $T = 25°$; $D = 78.54$

	Percentage Contribution of Successive Terms					
	1st approximation		3rd approximation		5th approximation	
x	log f	L	log f	L	log f	L
0.01	94.65	88.56	3.35	5.85	1.99	5.61
.02	90.75	80.95	5.77	9.63	3.48	9.41
.05	84.01	66.88	10.13	17.04	5.87	15.11
.10	80.13	60.85	13.43	22.00	6.41	17.17
.15	79.94	60.24	14.72	24.15	5.33	15.62
.20	81.15	60.64	15.07	26.00	3.80	13.36
.25	82.82	62.67	14.88	26.83	2.30	10.50
.30	84.60	65.16	14.38	27.19	1.01	7.66

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[17] Derived by Lange and Meixner by a single temperature differentiation of the Gronwall, La Mer and Sandved free energy equation (29) and neglecting the temperature variation of V (*Physik. Z.*, **30**, 670 (1929), see p. 675).

[18] Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931), where the values of various investigators are tabulated.

[19] La Mer, "Annual Survey of American Chemistry." Vol. V, 1930, pp. 12–13.

It is possible that the extended theory may not prove to be exact even when the higher approximations and the necessary dielectric data become available. In a recent note, Otto Halpern[20] claims that the statistical expressions for the average ionic potentials which are derived by the usual Debye method lead *in general* to expressions which do not obey the integrability relations of thermodynamics. This conclusion is necessary to explain the Gronwall[21] charging paradox. All expressions which contain *individual ionic diameters,* as well as higher approximations for ions of unsymmetrical valence type, do not conform to the integrability relations. Halpern's strictures would consequently invalidate all expressions based upon the Debye–Hückel theory of unsymmetric types and those for symmetric types in which the radius of the cation differs from that of the anion, except the limiting forms which are independent of "*a*." The numerical importance of these corrections is still unknown.

Summary

1. The electromotive force of the cell Cd (satd. amalgam, 11%) $CdSO_4$ (*m*), $PbSO_4$(s), Pb (satd. amalgam, 6%) has been measured at 0, 10, 20 and 30° for concentrations of cadmium sulfate of 0.0005, 0.001, 0.002, 0.005, 0.01 and 0.02 molal.

2. Using Wyman's value of the dielectric constant of water, and the Gronwall, La Mer and Sandved extension of the Debye–Hückel theory, the previous conclusion that "*a*" is 3.60 Å. for concentrations 0.0005 through 0.01 molal and independent of temperature from 0 to 30° is definitely confirmed.

3. The activity coefficients of cadmium sulfate are given for these concentrations and temperatures.

4. The following thermodynamic quantities have been computed for the process Cd(satd. Hg) + $PbSO_4$(s) = $CdSO_4$ (*m*) + Pb (satd. Hg) for the standard state of unit activity of cadmium sulfate for 15° (288.13°K.).

$E^\circ = 0.00905\ V$ $\Delta F^\circ = 417.6$ cal.

$(\partial E^\circ/\partial T)_p = -6.60 \times 10^{-4}$ $\Delta H^\circ = -9198$ cal.

$(\partial^2 E^\circ/\partial T^2)_p \cong -1.73 \times 10^{-5}$ $C_p^\circ \cong -229$ cal./deg.

5. The relative partial molal and integral heat contents of cadmium sulfate have been computed. Their concentration dependence is of the form demanded by the Gronwall, La Mer and Sandved theory. Exact comparison with the extended theory must await more precise determinations of the dielectric constant and its temperature derivatives at finite concentrations, as well as the calculations for the seventh and higher approximations for the calorimetric functions.

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(20) Halpern, *Phys. Rev.*, **43**, 495 (1933). Lars Onsager has independently reached a similar conclusion, *Chem. Rev.*, **13**, 73 (1933).

(21) Gronwall, La Mer and Sandved, Ref. 3, p. 367.

6. The partial molal heat capacity of cadmium sulfate is estimated to be approximately −200 cal./deg./mol. at 15°.

7. In the extended theory the equation for the activity coefficient converges more rapidly than the corresponding equation for the integral heat of dilution. Calculations of "a" based upon activity coefficients are consequently more reliable than those based upon equally accurate data of the heat of dilution.

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The Freezing Points of Aqueous Solutions. IV. Potassium, Sodium and Lithium Chlorides and Bromides

BY GEORGE SCATCHARD AND S. S. PRENTISS

The freezing points described in this paper were determined primarily as a part of a study of the freezing points of mixtures now being undertaken in this Laboratory.[1] They were made so early in order to give a comparison with the measurements on other salts, particularly the ammonium salts studied in our earlier paper; and to give a comparison of our temperature scale with that of other observers, most of whom have measured either potassium or sodium chloride. It is suggested that every freezing point apparatus be used to measure the freezing points of solutions of the easily purified potassium chloride; we believe in fact, that, for all but work of the very highest precision, the freezing point curve given in this paper would give a sufficient calibration in the range we have studied.

Recalibration of Apparatus.—In correlating the measurements previously reported[2] it was found that the precision of the measurements was about twice as good as anticipated for solutions more concentrated than 0.01 M, and that the greatest uncertainties lay in the purification of materials and the calibration of the apparatus. The apparatus was therefore carefully recalibrated. Although no change from our previous value was found greater than five hundredths of a per cent., the confirmation of our previous results warrants a brief description.

The resistance box used in the conductance measurements is frequently checked, and the most recent calibration is used. During the five years of its use there has been no change greater than 0.05%. In the first calibration of the thermocouple and the temperatures computed from it, a correction to the potentiometer varying from zero to 0.04% was ignored because it could not then be determined accurately, but is considered in the recalibration.

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[1] The references to earlier measurements on these salts are given in "International Critical Tables," Vol. IV, pp. 258–259 and in reference 3. After these measurements were completed one of us (G. S.) had the opportunity of seeing in the thesis of Damköhler (Munich, under Professor Fajans) the results of measurements with LiBr, NaBr and KBr. Those with potassium and sodium bromides are related to ours very much as are those of Karagunis, Damköhler and Hawkinson with KCl, which were used by Damköhler to calibrate his thermocouple. The measurements with LiBr show an additional difference approximately linear in the concentration and equal to $0.005/M$, our j values being more positive.

[2] Scatchard, Jones and Prentiss, THIS JOURNAL, **54**, 2690; Scatchard and Prentiss, *ibid.*, **54**, 2696 (1932).

The calibration of the thermocouple was carried out as before with additional measurements. The comparative measurements of the freezing points of salt solutions from −1 to −10° were made with two platinum resistance thermometers of the standard type used before, and with a third one with a very compact resistance oil. The correction factors for the exposed stem, determined as in the previous paper, are No. 103, 1.0020; No. 104, 1.0016; short coil, 1.0000. The determination of the temperature coefficient of electromotive force from these measurements alone requires extrapolation through the least certain of the measurements. To avoid this, the comparison was also made from +1 to +10° by filling one vessel with water alone and the other with an ice-water mixture, and regulating the temperature of the outer bath so that the temperature of the water vessel remained constant at the desired value. The correction factor for exposed stem was unity for all the thermometers.

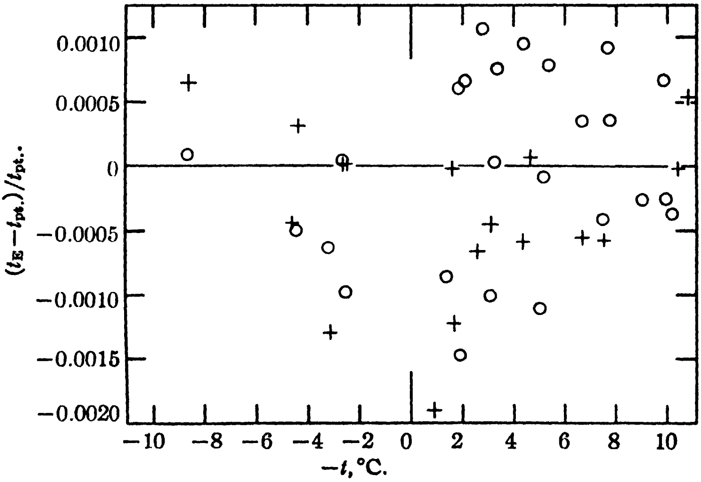

Fig. 1.—Calibration of thermocouple: ○, against large thermometers; +, against compact thermometer.

The relation between temperature and electromotive force was determined by the method of least squares. The measurements with a stem correction were considered half as precise as those without, and so given a weight of one quarter. In addition, the fact that the relative error decreases but the absolute error increases with increasing temperature was recognized by weighting each measurement as the reciprocal of the temperature difference. This is intermediate between giving the measurements equal weight as measurements of electromotive force and as measurements of its temperature coefficient. A two constant equation, explicit in either temperature or electromotive force, was found inadequate even over the range of twenty degrees. The equation used is $\Theta = 5.3857 \times 10^{-4}E + 3.38 \times 10^{-10}E^2 + 2.4 \times 10^{-15}E^3$. Θ is the temperature difference and E the electromotive force, both written positive for freezing points less than 0°. This equation gives temperature differences 0.03–0.04% larger than our former equation (with uncorrected electromotive forces), but does not warrant a revision of the results already published. Figure 1 shows the deviations of the measured values of Θ/E from this equation.

TABLE I

CONDUCTANCES AT 10°

M	*M/L*	*M*	*M/L*	*M*	*M/L*	*M*	*M/L*
KCl							
1.48296	12.781	0.38588	11.595	0.084451	10.651	0.004478	9.670
1.24054	12.575	.16411	11.038	.041269	10.308	.001439	9.501
0.97333	12.331	.11706	10.837	.040621	10.314	.000476	9.379
.83870	12.192	.098964	10.741	.012994	9.915	....	....
NaCl							
1.77709	18.429	0.62746	15.443	0.13891	13.509	0.003090	11.638
1.39591	17.461	.50148	15.057	.042195	12.601	.000965	11.438
1.11190	16.743	.35482	14.550	.026711	12.370	....	....
0.82681	16.000	.26452	14.178	.009428	11.934	....	....
LiCl							
1.87325	22.758	0.85314	18.819	0.14994	15.271	0.005727	13.066
1.36517	20.810	.67727	18.093	.078841	14.575	.001993	12.680
1.21237	20.223	.43647	17.004	.031174	13.859	.000774	12.626
1.02944	19.516	.26957	16.104	.015742	13.470	....	....
KBr							
1.29601	12.216	0.46754	11.073	0.046983	9.829	0.004512	9.402
1.07251	11.964	.28251	10.677	.020343	9.620	.001469	9.316
0.72135	11.497	.19939	10.452	.014042	9.551	....	....
.69490	11.457	.096075	10.085	.005370	9.420	....	....
NaBr							
1.41830	16.602	0.37751	14.076	0.10307	12.843	0.007195	11.537
1.13079	15.975	.34046	13.956	.053848	12.413	.003151	11.358
0.97107	15.604	.30817	13.840	.035359	12.180	.002179	11.292
.68019	14.918	.20002	13.403	.018742	11.881	.0010076	11.171
.53901	14.562	.160514	13.201	.007352	11.552	....	....
LiBr							
2.22009	22.023	0.73972	17.329	0.15765	14.778	0.008500	12.905
1.69499	20.369	.59056	16.801	.098129	14.308	.0024765	12.514
1.27569	19.064	.37793	15.955	.059407	14.146	.0008644	12.349
1.10305	18.523	.21755	15.156	.024885	13.338	....	....

TABLE II

FREEZING POINTS[a]

M		*M*	*j*	*M*	*j*	*M*	*j*
KCl							
A 0.001389	0.0044	B 0.056239	0.0593	E 0.28624	0.0972	F 0.68415	0.1144
B .002865	.0344	A .076739	.0675	F .35110	.1016	E .77852	.1170
A .006449	.0235	B .10646	.0742	E .40548	.1042	F .87671	.1193
B .011136	.0353	A .13558	.0795	B .48560	.1077	E .98203	.1216
A .016217	.0371	B .16926	.0851	E .51103	.1086	F 1.1624	.1245
B .027000	.0462	F .20277	.0889	F .56055	.1103	E 1.2455	.1254
A .038173	.0537	A .23141	.0923	E .62645	.1122		
NaCl							
A 0.000819	−0.0092	B 0.054924	0.0553	F 0.27394	0.0831	E 0.64857	0.0908
B .001866	+ .0092	A .078838	.0628	E .35492	.0863	F .72518	.0907
A .005120	.0192	B .10371	.0668	B .41547	.0881	E .80120	.0907
B .008605	.0265	A .12579	.0710	E .43370	.0884	F .90133	.0894
A .013540	.0334	B .15765	.0743	F .48597	.0892	E .99853	.0884
B .022648	.0445	F .18703	.0775	E .53070	.0899	F 1.1540	.0862
A .033489	.0468	A .22318	.0803	F .59159	.0902	E 1.2774	.0845
LiCl							
C 0.000815	0.0125	B 0.028830	0.0442	F 0.22480	0.0552	F 0.60053	0.0244
B .001000	.0369	A .041929	.0484	A .25602	.0543	E .66599	.0177
A .001388	.0246	B .062321	.0534	F .29320	.0516	F .75093	.0076
C .001889	.0215	A .083317	.0552	E .35012	.0473	E .82305	− .0011
B .003350	.0263	B .10807	.0573	B .39572	.0445	F .91361	− .0119
C .003706	.0233	A .13317	.0577	E .43607	.0398	E 1.0050	− .0232
A .005982	.0264	B .15304	.0583	F .49181	.0351	F 1.1196	− .0370
B .010810	.0334	F .19001	.0567	E .54212	.0296	E 1.2458	− .0541
A .017113	.0393						
KBr							
A 0.000407	0.0016	A 0.039203	0.0530	F 0.19254	0.0851	F 0.57808	0.1086
B .001077	.0155	B .054501	.0590	E .22465	.0883	E .64269	.1101
A .001824	.0130	A .081145	.0660	F .26581	.0924	F .71866	.1122
B .003996	.0235	B .099459	.0710	B .33814	.0982	E .80717	.1135
A .006101	.0217	A .12646	.0756	E .40910	.1017	F .97516	.1170
B .011641	.0327	B .13729	.0778	F .46834	.1046	E 1.0203	.1177
A .016397	.0363	E .15791	.0804	E .50792	.1061	F 1.2086	.1200
B .026573	.0447	A .17833	.0835				
NaBr							
C 0.000780	0.0268	B 0.023990	0.0352	A 0.18545	0.0675	E 0.62685	0.0720
A .001558	.0086	A .035356	.0419	F .23609	.0701	F .69944	.0707
C .002859	.0154	B .054396	.0484	E .27647	.0713	E .77676	.0684
B .003263	.0025	A .077400	.0548	B .33054	.0727	F .87964	.0663
A .005966	.0194	B .098178	.0580	E .39038	.0732	E .96594	.0634
B .010280	.0202	A .12220	.0616	F .43827	.0734	F 1.0883	.0610
C .010303	.0279	B .14571	.0642	E .50805	.0733	E 1.2071	.0573
A .015339	.0302	F .16169	.0662	F .56626	.0728		
LiBr							
A 0.000624	0.0253	A 0.076987	0.0474	B 0.31767	0.0352	E 0.69589	−0.0135
B .003072	.0189	B .099525	.0483	E .36432	.0294	F .75678	− .0223
A .006586	.0242	A .12791	.0482	F .40353	.0253	E .82116	− .0311
B .010013	.0268	B .15753	.0482	E .45909	.0188	F .91251	− .0455
A .015918	.0335	F .18709	.0461	F .52094	.0106	E .98507	− .0561
B .026640	.0377	A .23072	.0431	E .57843	.0032	F 1.0694	− .0692
A .036837	.0424	F .27647	.0386	F .62698	− .0040	E 1.1715	− .0855
B .055585	.0445						

[a] The letters indicate the series. Series A-C were run with increasing concentration; series E–F with decreasing concentration.

Experimental Results.—The freezing points were measured by the "equilibrium method" and the concentrations determined by conductance just as described in the previous papers[2], except that the nitrogen was always passed through an ice–water mixture to cool it and saturate it with water vapor before it was bubbled through the solution.

Table I contains the measurements of the conductance; M is the moles of salt per kilogram water and L the specific conductance. Table II contains the measured freezing points expressed as the Lewis and Randall

TABLE III

j VALUES OF THE ALKALI CHLORIDES AND BROMIDES

M	Lim. law	KCl	NaCl	LiCl	KBr	NaBr	LiBr
0.001	0.0118	0.0111	0.0108	0.0124	0.0111	0.0103	0.0107
.002	0167	.0154	.0148	.0171	.0152	.0136	.0145
.005	.0264	.0233	.0222	.0254	.0230	.0195	.0212
.01	.0374	.0315	.0297	.0328	.0309	.0259	.0277
.02	.0529	.0417	.0388	.0404	.0407	.0341	.0347
.05	.0836	.0586	.0537	.0507	.0567	.0473	.0439
.1	.1182	.0734	.0663	.0568	.0707	.0585	.0482
.2	.1672	.0890	.0785	.0570	.0860	.0683	.0452
.3	.2047	.0978	.0843	.0515	.0950	.0720	.0366
.4	.2364	.1038	.0876	.0434	.1012	.0733	.0258
.5	.2643	.1082	.0895	.0341	.1056	.0733	.0135
.6	.2897	.1119	.0904	.0239	.1090	.0723	.0002
.7	.3127	.1149	.0907	.0129	.1117	.0704	− .0138
.8	.3343	.1175	.0902	.0015	.1138	.0682	− .0283
.9	.3546	.1199	.0896	− .0104	.1157	.0658	− .0434
1.0	.3738	.1218	.0884	− .0226	.1173	.0631	− .0586
1.1	.3920	.1236	.0871	− .0350	.1187	.0603	− .0741

TABLE IV

VALUES FOR $-\text{LOG}\ \gamma'$ FOR THE ALKALI CHLORIDES AND BROMIDES

M	Lim. law	KCl	NaCl	LiCl	KBr	NaBr	LiBr
0.001	0.0154	0.0148	0.0145	0.0159	0.0148	0.0143	0.0144
.002	.0218	.0206	.0201	.0223	.0205	.0191	.0199
.005	.0344	.0317	.0306	.0343	.0313	.0282	.0298
.01	.0487	.0434	.0416	.0463	.0428	.0377	.0400
.02	.0689	.0587	.0557	.0605	0578	.0503	.0525
.05	.1089	.0857	.0804	.0830	.0839	.0721	.0720
.1	.1540	.1121	.1039	.1017	.1091	.0928	.0877
.2	.2178	.1430	.1309	.1192	.1392	.1161	.1008
.3	.2667	.1632	.1476	.1262	.1590	.1300	.1041
.4	.3080	.1782	.1596	.1285	.1737	.1394	.1032
.5	.3444	.1903	.1690	.1281	.1855	.1465	.0996
.6	.3775	.2006	.1764	.1259	.1955	.1516	.0943
.7	.4074	.2093	.1824	.1220	.2038	.1554	.0875
.8	.4356	.2171	.1872	.1175	.2111	.1583	.0798
.9	.4620	.2241	.1915	.1117	2177	.1606	.0712
1.0	.4870	.2302	.1948	.1055	.2236	.1622	.0621
1.1	.5107	.2360	.1977	.0988	.2290	.1634	.0524

function $j = 1 - \Theta/3.716\ M$ (Θ is the freezing point depression). The smoothed values of M/L and of j were obtained by drawing smooth curves through the deviations of the experimental results from approximate analytical functions of the same types as those used in the earlier work. For M/L the average deviations of the experimental points from these curves are slightly more than one in the last place given. For j the average deviation for concentrations greater than 0.01 M is approximately three in the last place given. For more dilute solutions the average deviation corresponds to about 0.00003°. Table III contains the smoothed values of j at rounded concentrations, and Table IV the corresponding values of log γ'. γ' is the activity coefficient (moles per kilogram of water) uncorrected for heat of dilution, etc.

For the chlorides the water used was distilled from a new Kraus type still, and the ice used in some of the runs was prepared from this water. No effect of these changes could be noted.

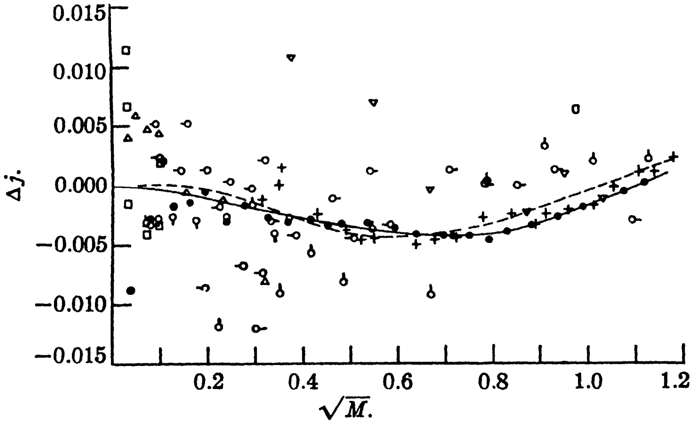

Fig. 2.—Δj Values for KCl; $\Delta j = j - [(0.3738\sqrt{M})/(1 + 1.7\sqrt{M})] + 0.0149\ M$; solid line, Scatchard and Prentiss; broken line, Spencer; ●, Scatchard and Prentiss; +, Jones and Bury; ♀, Adams; ȯ, Menzel; ⟜, Jahn; ⊸, Karagunis, Hawkinson and Damköhler; △, Flügel; ▽, Rivett; □̇, Rodebush; □, Hovorka and Rodebush.

Potassium Chloride.—A C. P. product was twice crystallized from conductivity water and dried for ten hours at 250°. The stock solution was made up by weighing this salt. The filled circles in Fig. 2 show the results plotted as deviations Δ_j in the empirical equation

$$= \frac{0.3738\sqrt{M}}{1 + 1.7\sqrt{M}} - 0.0149\ M + \Delta_j$$

The smooth curve which we draw through these results is shown by the full line. Some of the earlier measurements are included in the figure. Those of Jones and Bury, which are probably the best in the more concentrated range, agree excellently with our curve. The broken line represents the smooth curve determined by Spencer[3] from these earlier

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(3) Spencer, THIS JOURNAL, 54, 4490 (1932).

measurements. We believe that the full curve, determined from our own measurements alone, fits the earlier measurements as well as the curve determined from them; but we consider it much more important that Spencer's curve fits our experimental measurements better than it does those from which it was determined, and that the difference between his curve and ours is always less than one part per thousand. There is a greater discrepancy in the values of γ', apparently due to some inaccuracy in his integration.

Sodium Chloride (C. P.) was dissolved in water, precipitated with hydrogen chloride gas, washed, dried at 200° and fused. The stock solution was made by weighing this salt.

Lithium Chloride (C. P.) was dissolved in water and added to a solution of ammonium carbonate saturated with ammonia. The precipitate was washed and dissolved in reagent hydrochloric acid. Lithium carbonate was again precipitated with ammonium carbonate as before, the precipitate washed, dried at 270° and then fused. After dissolving in hydrochloric acid the solution was titrated to a *P*H of 6.6 with brom thymol blue with boiling to expel carbon dioxide. The concentration of the stock solution was determined by evaporation and conversion to lithium sulfate.

Potassium, Sodium and Lithium Bromides (C. P. or reagent) were each crystallized once from conductivity water. The concentrations of the stock solutions were determined gravimetrically as silver bromide. These solutions were analyzed for chloride by the method of Berg.[4] In each case 40 cc. of 0.1 *M* solution was oxidized with 0.05 *M* potassium bromate in the presence of acetone, silver nitrate was added and the precipitate compared in Nessler tubes with known samples of silver chloride. The amounts of chloride found were: KBr, 0.25%; NaBr, 0.3%; LiBr 0.25%. Flame tests of the potassium bromide showed, as for potassium and lithium chlorides, the absence of sodium. The lithium bromide appeared by the same test to contain about 0.2% NaBr. By our method of analysis 0.25% chloride gives a total concentration 0.06% too small and sodium in place of lithium makes no difference except in the magnitude of the deviations. Since the method of testing for chloride is almost certain to give high results, we do not believe that our results are in error due to impurities by more than one part per thousand.

Discussion.—These measurements require very little discussion. Just as in the earlier less precise measurements, the bromides all show greater deviations from the limiting law than the corresponding chlorides, and the deviations for salts of the same anion increase in the order potassium, sodium, lithium with the exception of very dilute solutions of lithium chloride. Our most probable curve for this salt appears to cross the curves of sodium and potassium chlorides and the limiting law. The intersections all occur in very dilute solutions where the curves lie close together and where the percentage accuracy is not very great, so that we cannot be sure that the effect is greater than the experimental error. Such an effect should be expected for small ions from the Bjerrum–Gronwall, La Mer and Sandved correction, but the size required to give it if only the charge-charge effect be considered is smaller than the dimensions of the ions in the crystal lattice and the large deviations in the more concentrated solutions indicate that a much smaller size would be necessary to show such an effect.

We have now studied potassium, sodium and lithium nitrates, chlorides and bromides, corresponding to the three ammonium salts which gave large "humps" in the j curves with well marked positive deviations from the theoretical limiting law. Eight of the alkali salts show no positive deviation at all, and that of lithium chloride is less than one-tenth of that of the ammonium salts. The behavior of the ammonium salts is still unexplained, but the present work shows conclusively that it is not due to a systematic error in our measurements. To make doubly sure on this score, since ammonium bromide showed the largest "hump," the alkali bromides were purified and their concentrations were determined by the same method as had been used for the ammonium salt.

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[4] Berg, *Z. anal. Chem.*, **69**, 342 (1926).

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[CONTRIBUTION FROM THE PENNSYLVANIA SALT MANUFACTURING COMPANY CHEMICAL RESEARCH DEPARTMENT]

Addition of 8-Hydroxyquinoline by Thorium and Uranium 8-Hydroxyquinolates

BY FRANCIS J. FRERE

Introduction

F. Hecht and W. Reich-Rohrwig[1] have outlined an analytical procedure for the determination of thorium and uranium by means of 8-hydroxyquinoline. It was stated that uranium formed a compound of the formula $UO_2(C_9H_6NO)_2 \cdot C_9H_6NO$, which was stable up to about 200°.

As regards thorium, Hecht and Reich-Rohrwig[1] stated that this element formed a compound containing water of crystallization which did not start to dehydrate until at about 155°, and at 160 to 170° lost its water of crystallization rapidly and could be dried to constant weight at this temperature. The dried precipitate was dissolved and brominated and was found to contain four moles of 8-hydroxyquinoline, from which it was concluded that thorium formed a compound of the formula $Th(C_9H_6ON)_4$.

Hecht and Reich-Rohrwig later observed that when brominating the thorium precipitate, without drying, somewhat high results were obtained. This was claimed to have been overcome by washing the precipitate with 25% alcohol.

An investigation of this work found some of the above statements in error and has led to a rather interesting phenomenon.

Experimental

Materials Used.—C. P. reagent grade thorium nitrate and uranyl acetate were used in these experiments. The thorium nitrate solution was standardized by precipitating as oxalate, igniting and weighing as the oxide. The uranyl acetate solution was standardized by reducing in a Jones reductor and titrating with potassium permanganate. Pipets and burets certified by the U. S. Bureau of Standards were used throughout this work.

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[1] Hecht and Reich-Rohrwig, *Monatsh*, **53–54**, 596 (1929).

A series of experiments was first made in order to determine whether or not thorium 8-hydroxyquinoline formed a compound containing water of crystallization. The following general procedure was used throughout for precipitating both thorium and uranium.

The solution was treated with 4 to 5 ml. of 2 *N* acetic acid heated to 90° and an excess of a 2.5% solution of 8-hydroxyquinoline was added; the solution was heated to boiling and about 15 ml. of 2 *N* ammonium acetate was added. After allowing to cool to room temperature, the precipitate was filtered on a weighed Gooch crucible, washed with cold water, and dried for two hours at 130 to 140°. The precipitate was then dissolved in hydrochloric acid and the quinolate titrated with a potassium bromide-bromate solution.[2] It seems quite obvious from the results given in Table I that thorium does not form a hydrated salt with 8-hydroxyquinoline and that the high results obtained by Hecht and Reich-Rohrwig cannot be attributed to this cause.

TABLE I

COMPOSITION OF THORIUM 8-HYDROXYQUINOLINE PRECIPITATE

Precipitate, g.	0.1015	0.1012	0.1024	0.1010	0.1012
C_9H_6NOH found, g.	.0744	.0745	.0751	.0744	.0744
Total found, g.	.1015	.1016	.1022	.1015	.1015
Diff., g.	.0	+ .0004	− .0002	+ .0005	+ .0003

TABLE II

DETERMINATION OF THORIUM RESULTS CALCULATED ON THE BASIS OF $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$

ThO_2 added, g.	0.0062	0.0062	0.0062	0.0123	0.0123	0.0123	0.0309	0.0309
ThO_2 found, g.	.0062	.0061	.0061	.0123	.0123	0.0122	.0309	.0310

The amount of 8-hydroxyquinoline which combines with thorium and uranium was determined by precipitating both cations as outlined above, dissolving the precipitates in hydrochloric acid and titrating with potassium bromate. It will be seen from Table II and Table III that both elements combine quantitatively with one additional mole of 8-hydroxyquinoline in excess of their normal valence.

Washing the thorium precipitate with 25% alcohol, as recommended by Hecht and Reich-Rohrwig, proved unsuccessful and no reliable results were obtained.

TABLE III

DETERMINATION OF URANIUM: RESULTS CALCULATED ON THE BASIS OF $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$

U_3O_8 added, g.	0.0056	0.0056	0.0056	0.0112	0.0112	0.0112	0.0279	0.0279
U_3O_8 found, g.	.0056	.0056	.0055	.0111	.0111	.0111	.0278	.0278

Another series of experiments was made in order to determine the stability of the thorium and uranium 8-hydroxyquinolates at various temperatures and to find, if possible, at what temperature the additional mole of 8-hydroxyquinoline could be driven off. Both compounds were found to be quite stable at 100 to 110°. At 130 to 140° the thorium salt slowly decreased in weight while the uranium salt remained practically constant. When the temperature was raised to 160 to 170°, the thorium salt completely lost the additional mole of 8-hydroxyquinoline in about three hours, and, upon further heating at this temperature, continued slowly to decrease in weight. The uranium salt slowly decreased in weight at 160 to 170°, but at 200° the additional mole of 8-hydroxyquinoline was liberated in about two hours. The residue consisting of the compound containing two moles of 8-hydroxyquinoline was found to be quite stable at this temperature.

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[2] R. Berg, *Pharm. Z.*, **71**, 1542 (1926). See also Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, New York, 1929, Vol. II.

It was noted also that the precipitates had changed from their original color. The thorium precipitate changed from an orange-red to a light yellow and the uranium changed from a deep brick-red to an olive-green.

An attempt was now made to determine whether or not these regenerated precipitates would again recombine with 8-hydroxyquinoline. Known quantities of each precipitate were treated with a few ml. of a 2.5% solution of 8-hydroxyquinoline and digested at a low heat on the hot-plate. It was observed that upon slight warming the precipitates rapidly changed back to their original red color, this being particularly noticeable of the uranium salt. The thorium salt did not recombine with the same degree of ease, and it was found necessary to increase the concentration of 8-hydroxyquinoline from about 3 ml., as in the case of uranium 8-hydroxyquinoline, to about 10 ml. The time of digestion was also slightly longer. However, in no case did it exceed more than ten to fifteen minutes.

It will be seen from Tables IV and V that the recombination of 8-hydroxyquinoline goes nearly to completion. Perhaps the slight differences may be due to inefficient wetting of the precipitates.

TABLE IV

ADDITION OF 8-HYDROXYQUINOLINE BY $Th(C_9H_6NO)_4$

$Th(C_9H_6NO)_4$ taken, mml.	C_9H_6NOH before addition, mml.	C_9H_6NOH after addition, mml.	C_9H_6NOH added, mml.	Conversion $Th(C_9H_6NO)_4$ to $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$, %
0.0234	0.0937	0.1135	0.0189	96.92
.0469	.1877	.2272	.0395	96.84
.0933	.3731	.4514	.0783	96.78
.1244	.4975	.6054	.1079	97.34

TABLE V

ADDITION OF 8-HYDROXYQUINOLINE BY $UO_2(C_9H_6NO)_2$

$UO_2(C_9H_6NO)_2$ taken, mml.	C_9H_6NOH before addition, mml.	C_9H_6NOH after addition, mml.	C_9H_6NOH added, mml.	Conversion $UO_2(C_9H_6NO)_2$ to $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, %
0.0442	0.0833	0.1277	0.0394	96.37
.0883	.1767	.2577	.0790	96.49
.1325	.2650	.3915	.1265	98.49
.1766	.3533	.5141	.1608	97.00

Results shown in Tables IV and V are the mean of duplicate determinations.

Evidence for an Addition Compound.—Portions of the thorium and uranium 8-hydroxyquinolates which had been previously dried at 100 to 110° were placed in a closed vessel connected to a condenser tube and heated carefully at 170 and 200°, respectively. The sublimation products which were collected gave a melting point of 73 to 74°, which was the same as that of the 8-hydroxyquinoline. This sublimed salt was used for precipitating thorium and uranium and both gave precipitates identical with the original.

The above evidence seems to be sufficient to show that thorium and uranium form molecular complexes and, according to Werner's coördination formula theory, the additional mole of 8-hydroxyquinoline is held by secondary valence.[3]

It may also be noteworthy to mention that of the many elements which form precipitates with 8-hydroxyquinoline, thorium and uranium are the only two known which form an addition compound.

Summary

1. It has been shown that thorium and uranium 8-hydroxyquinolates form an addition compound with 8-hydroxyquinoline.

2. It has been shown that the additional mole of 8-hydroxyquinoline can be driven off by heating and that it will again recombine to nearly its former value.

3. An explanation of these phenomena on the basis of Werner's theory of secondary valence seems plausible.

(3) A. Werner, "New Ideas on Inorganic Chemistry." Translated from second German ed. by E. P. Hedley, Longmans, Green and Co., New York, 1911.

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[CONTRIBUTION FROM THE ALABAMA EXPERIMENT STATION]

Magneto-optic Nicol Rotation Method for Quantitative Analysis of Calcium

BY EDNA R. BISHOP, C. B. DOLLINS AND IRENE G. OTTO

The magneto-optic method[1] of analysis detects the presence of minute traces of a compound regardless of the presence of other compounds. A quantitative method[2] for the determination of calcium depending on dilutions has been described. It offers a means of analysis of samples containing less calcium than could be detected by other methods, but the determination is slow and requires a high degree of skill to operate the apparatus and great care to prevent contamination.

Allison and Murphy[3] early investigated the effect of concentration on the amount that the analyzing nicol could be rotated and the minima still be seen. They found an increase in the angle of rotation with increase in concentration of the solution examined but the variation in angle was less than 2° for a change in concentration from 10^{-11} to 10^{-3} g./cc.; hence, it did not lend itself to quantitative use. Similar determinations were made recently with like results.

In the meantime, however, Allison, Christensen and Waldo[4] predicted and found that the characteristic minima could also be produced if the current was passed through both coils of the apparatus (Fig. 1) in the same direction, with the analyzing nicol set parallel to the polarizing nicol. This arrangement was investigated and found suitable for quantitative analysis by nicol rotation.

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[1] Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930); Allison, *Ind. Eng. Chem., Anal. Ed.*, **4**, (1932).

[2] Bishop and Dollins, THIS JOURNAL, **54**, 4585 (1932).

[3] Work unpublished.

[4] Allison, Christensen and Waldo, *Phys. Rev.*, **40**, 1052 (1932).

Arrangement of Apparatus.—The optical train of the present arrangement is shown diagrammatically in Fig. 1. Light from the magnesium spark G is rendered parallel by the lens L and then passes through the color filter F, control nicol N_3, polarizing nicol N_1, cell containing carbon disulfide in the helix B_1, cell containing the solution studied in helix B_2, and analyzing nicol N_2. N_3 is mounted so that it can be rotated at will to give the light intensity at which minima can be most easily detected. N_2 is mounted in a circle calibrated to hundredths of a degree in a counterclockwise direction and is set crossed with respect to N_1 at 90° on the circle. The current flows counterclockwise through both B_1 and B_2.

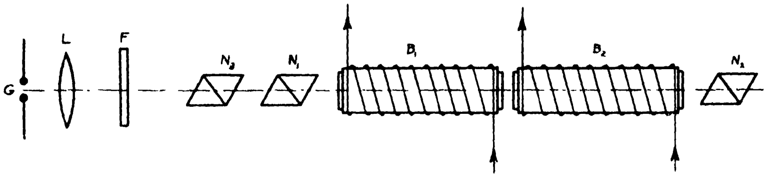

Fig. 1.—Optical train of magneto-optic apparatus for quantitative analysis by nicol rotation.

Production of Maxima and Minima.—At the characteristic scale settings of the trolley, solutions of compounds in B_2 produce maxima of light intensity when N_2 is set at 90° and minima of light intensity when it is set at 0°. If N_2 is rotated from either position, the maxima or minima persist through considerable angles. The amount of rotation of N_2 possible before the maxima or minima disappear is dependent on the concentration of the compound in B_2 but varies over a wider angle when N_2 is rotated from a position parallel to N_1 than from a position crossed with respect to N_1. Minima are more easily read than maxima and therefore the former are used for quantitative work.

It has not been possible to make any absolute measurements of light intensity, but Fig. 2 shows diagrammatically the apparent manner of variation of light intensity with nicol settings. The solid curve represents the effect produced with a concentrated solution and the dotted curve with a dilute one. Minima can be detected only when the light intensity differs from normal intensity, indicated by the line AB, by a definite amount. This amount, however, is characteristic of the individual eye and may correspond to a reduction to MN for one eye and to XY for another and hence produces the individual differences shown in Fig. 3. After passing this threshold value, the eye detects the minimum but is not capable of distinguishing the amount of change from normal, so that as soon as the threshold value of concentration or angle is passed the eye detects no change in the appearance of the minima. We are unable to interpret these results in terms of a Faraday rotation or to offer any other theoretical explanation.

With the arrangement shown in Fig. 1 and N_2 set parallel to N_1, the sensitivity or lowest concentration of calcium that can be detected is 3.74×10^{-12} g. of Ca/cc., which is the same as that previously reported[2] with current in the coils opposing and nicols crossed.

Calibration Curve.—Calcium chloride solutions ranging in concentration from 3.83×10^{-12} of aqueous solution to 0.089 g. of Ca/cc. of solution were prepared from stock solutions in which the calcium had been determined by permanganate titration. The limiting angle through which N_2 could be rotated and minima read was determined for each. To do this, N_2 was rotated clockwise 10° at a time from zero until no minima were observed. This 10° range was then studied until two points were found 1° apart one of which would and one would not give minima. N_2 was set at the smallest angle where minima were not visible and rotated by a fine adjustment screw until each minimum just appeared. The angle for each isotope was read and the average of these two values was used. The results are shown in Curve I and Curve II, Fig. 3.

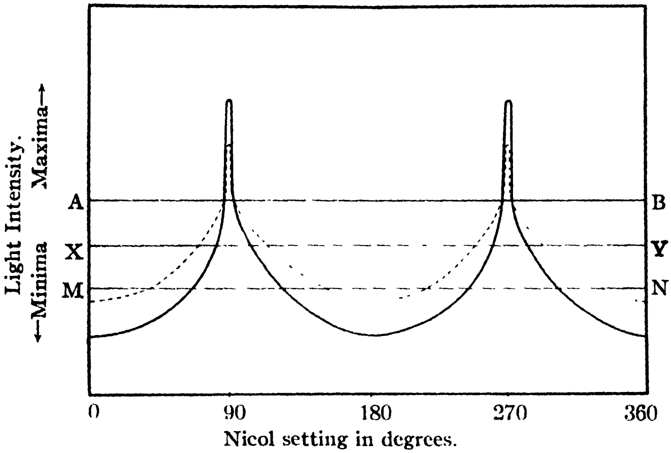

Fig. 2.—Effect of nicol rotation on maxima and minima: solid curve, concentrated solution; dotted curve, dilute solution; AB, normal light intensity; XY and MN, light intensity at which a given eye sees minima.

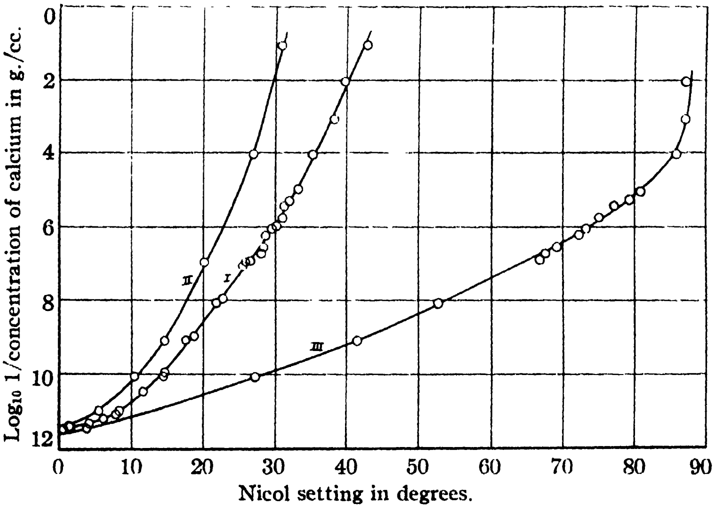

Fig. 3.—Calcium calibration curves: Curve I, direction of nicol rotation opposite to flow of current (Dollins); Curve II, direction of nicol rotation the same as flow of current (Dollins); Curve III, direction of nicol rotation opposite to flow of current (Otto).

Each point on the curve represents the average of at least four readings which were made on at least two different days and with all parts of the apparatus completely readjusted. Settings of N_2 were reproducible to 0.20° or less except for concentrations of 1×10^{-3} g. of Ca/cc. or greater where the variation increased to one degree. Hence, if a preliminary examination showed a calcium content in this range a dilution was made and the angle of rotation determined for the diluted solution which comes on a more accurate part of the curve. A new circle and nicol were installed during the progress of the work but produced no change in the results obtained.

Extensive determinations were also made starting with the minima just visible and rotating the nicol until they could not be seen. It was harder to recognize the point of disappearance than of appearance of the minima and variations as great as 0.50° were obtained.

If either the direction of the current in the coils or the direction of rotation of the nicol is reversed, the angle of rotation for a given concentration becomes less as is shown in Curve II of Fig. 3. Hence, it is important that the nicol should be rotated in a direction opposite to that of the flow of the current.

Variation of the capacity or resistance of the circuit or of light intensity does not affect the results as long as these factors are kept within the limits that produce easily detected minima.

Effect of the Presence of other Compounds.—The presence of excess chloride, nitrate, sulfate, phosphate, hydrogen, magnesium, sodium or ammonium did not affect the limiting angle at which the minima could be detected, and in the presence of an excess of all four cations the minima of each of the four calcium compounds were read at the same angle. These results are similar to those found for the dilution method.[3] Experiments with nicol rotation also checked the former results[3] that the rate of solution of calcium from the glass is not great enough to interfere with the use of the method.

Personal Factor.—The angle of rotation, however, depends not only on the concentration but on the observer. Dr. Fred Allison, Mr. R. E. Wingard, Mr. Roy Goslin and Mr. Louis Baisden have also made a considerable number of determinations of this nature. Each finds consistent and reproducible results, but at a different circle reading for a given concentration, so that each observer must determine his own calibration curve. This personal variation is shown in Fig. 3, where Curves I and III were obtained in exactly the same manner by Mr. C. B. Dollins and Miss Irene Otto, respectively.

Determination of Calcium in Vegetables.—Analyses were made of samples of plant ash prepared as previously described.[3] The solutions were then analyzed by nicol rotation. For example, in solution Number 56, Mr. Dollins saw the minima at 30° but not at 31°. The nicol was then set at 31° and he turned the fine adjustment screw as he

TABLE I

THE PERCENTAGE OF CALCIUM IN VEGETABLES AS DETERMINED BY DIFFERENT METHODS

			Magneto-optic determinations, Nicol rotation							
		Dried vegt./ 10^3 cc.	Nicol rotation in degrees		Concn. g. Ca/10^6 cc.		Calcium, %		Dilution calcium, %	Permanganate titration calcium, %
Vegetable	Soln.		Dollins	Otto	Dollins	Otto	Dollins	Otto		
New Zealand spinach	56	0.1489	30.43	74.67	1.38	1.32	0.926	0.885	0.973	0.900
	63	.1282	30.20	74.41	1.15	1.22	.900	.954	.994	
Turnip tops	57	.1187	31.25	76.53	2.54	2.29	2.13	1.93	2.01	2.04
	55	.1607	31.59	77.56	3.31	3.09	2.06	1.93	2.00	
Chinese cabbage	1	.0818	30.70	75.28	1.68	1.58	2.05	1.93	..	1.88
	88	.1170	31.04	76.45	2.19	2.24	1.87	1.92	..	
Onion tops	59	.0670	28.86	71.15	0.454	0.447	0.676	0.667	..	0.663
	79	.0902	29.36	72.14	.631	.616	.700	.684	..	

moved the trolley over 18.66 until the minimum just appeared. The reading of the circle was 30.53. He then moved the trolley over 18.44 as he turned the screw until that minimum just appeared which was at nicol setting 30.33. This was repeated four times and the average value was used. The log of the reciprocal of the concentration which corresponded to this nicol rotation was read from the calibration curve. The concentration and percentage composition were then calculated in the usual manner. Table I shows the results obtained by two different observers employing this method, those obtained by the magneto-optic dilution method[2] and by permanganate titration. All samples were unknown to the observers and were designated simply by number. All circle settings were made by the second worker so that the observer merely decided whether minima could be seen or not without knowledge of the nicol setting. Duplicate determinations by the same or different observers check each other and the values obtained by permanganate titration within 10% error.

Limitations.—The actual observing time necessary to make a determination after preparation of the solution was about fifteen minutes. The eye, however, will not stand such steady observing and it was found necessary to take about an hour to a determination and four determinations a day were as much as one person could make. Two workers are needed, one to observe minima and one to watch the trolley movement. Considerable practice is necessary to obtain adequate skill in the operation of the apparatus. The determination of the individual calibration curve is a slow, tedious process. The error in this method is greater than that obtained by conventional chemical methods for solutions whose concentration is adapted to their use.

Advantages.—The magneto-optic determination of calcium, however, is useful over a very wide range of concentrations and at lower concentrations than any other known method. The solution analyzed undergoes no change. Complex mixtures may be analyzed without preliminary separations as there is no interference from the presence of any substance tested.

Possibilities.—Since none of the compounds tested affects the determinations and since the angle of rotation is the same for a given amount of calcium in every calcium compound studied, it seems probable that this method may be used for the determination of calcium in any type of sample by employing appropriate means for the preparation of a clear transparent solution.

Preliminary work supports the possibility that the same technique may be employed for the quantitative determination of any compound. Three requirements must be fulfilled. First, the location of the minima of the compound to be determined must be known. Those of many inorganic compounds are known and the approximate location of others can be predicted from equivalent weight relations and hence these can be located with comparative ease. The minima of very few organic compounds have been located and there is as yet little basis for predicting their location, so this may be quite a laborious task. Second, a calibration curve for the angle of extinction *vs.* concentration must be prepared from solutions of known concentrations by the person who is to make the determinations. Third, the substance to be determined must yield a clear solution that will transmit light.

We wish to express our appreciation to Dr. Fred Allison for the use of his apparatus and for putting at our disposal the unpublished data of work which he did with Mr. Edgar J. Murphy, Mr. R. E. Wingard and Mr. Roy Goslin. We also wish to thank Dr. W. N. Arnquist and Mr. J. H. Christensen for helpful discussions and suggestions concerning the plotting of the curves.

Summary

A magneto-optic quantitative method for the determination of calcium by rotation of the analyzing nicol is described.

The range of concentration for which the method is best adapted is 3.74×10^{-12} to 1×10^{-3} g. of Ca/cc. More concentrated solutions are diluted to this range.

The angle through which the analyzing nicol can be rotated and the minima still persist depends on the concentration of calcium in the solution and on the observer. The results are not affected by the presence of any of the foreign substances tested, *viz.*, magnesium, sodium, ammonium, hydrogen, sulfate, nitrate or phosphate. Variations of the capacity and resistance of the circuit or of the light intensity used do not affect the results provided the adjustment of these factors is within the limits to produce good minima.

The limiting angle of rotation is the same for a given calcium concentration whether the minima are read for the chloride, sulfate, nitrate or phosphate.

Nicol settings are reproducible within a maximum variation of 0.20° under optimum adjustment of the apparatus and the concentration range employed.

Duplicate determinations by the same or different observers check each other and the values obtained by permanganate titration within 10%.

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[CONTRIBUTION FROM THE ALABAMA EXPERIMENT STATION]

Manganese Isotopes

BY IRENE G. OTTO AND EDNA R. BISHOP

Before entering upon a study of the quantitative determination of small amounts of manganese by the magneto-optic method,[1] it was necessary to locate the position of the minima of manganese compounds on the wire-path scale. This location can be accurately predicted since it is a function of the equivalent weight of each constituent element. This means also that elements having more than one valence will have minima in different scale regions for each valence and that only elements having similar equivalent weights can possibly be confused with each other.

Experimental

Solutions for examination by the magneto-optic method were prepared by dissolving C. P. manganous salts in water freshly redistilled from an all Pyrex still. Examination of the appropriate regions of the wire-path scale showed seven minima for each compound as shown in Table I.

The nicol rotation method[2] was employed in order to show whether these minima were due to isotopes of manganese or to contaminations and, if to manganese isotopes, to establish their order of abundance. The greatest rotation of the analyzing nicol at which each minimum could be seen is shown in Table I. Since these angles are close together for all compounds, they must either be due to manganese isotopes which follow each other in close succession because of mutual influence,[3] or to a contamination which has a weight that gives minima in these regions of the scale and is consistently present at approximately the same concentration as the manganese salts studied. The latter is highly improbable in several C. P. salts.

To test further whether these minima all belonged to manganese, hydrogen peroxide was added to the manganous phosphate solution, whereupon its seven minima disappeared while seven minima in a scale region

TABLE I

SCALE READINGS AND NICOL ROTATION OF MANGANESE ISOTOPES IN VARIOUS COMPOUNDS

Order of abundance	$MnSO_4$ Scale reading	$MnSO_4$ Nicol rotation	$MnCl_2$ Scale reading	$MnCl_2$ Nicol rotation	$Mn_3(PO_4)_2$ Scale reading	$Mn_3(PO_4)_2$ Nicol rotation	$MnPO_4$ Scale reading	$MnPO_4$ Nicol rotation
2	13.25	46°58′	19.01	58°42′	24.45	66°1′	21.43	66°18′
7	13.38	44°56′	19.08	56°10′	24.64	64°17′	21.58	64°21′
5	13.54	45°56′	19.13	57°7′	24.86	64°59′	21.63	65°02′
1	13.69	47°27′	19.22	59°13′	25.04	66°22′	21.70	66°41′
4	13.85	46°18′	19.31	57°34′	25.25	65°18′	21.78	65°29′
3	14.02	46°50′	19.45	58°18′	25.43	65°42′	21.85	65°50′
6	14.14	45°32′	19.54	56°40′	25.64	64°37′	21.91	64°35′

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(1) Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

(2) Bishop, Dollins and Otto, *ibid.*, **55**, 4365 (1933).

(3) Allison, *Ind. Eng. Chem., Anal. Ed.*, **4**, 9 (1932); *Science*, **77**, 494 (1933).

appropriate to manganic phosphate appeared. Perchloric acid was added and all these minima disappeared. A few drops of oxalic acid solution were added and both sets of minima became visible. After a second addition of oxalic acid, however, the minima attributed to manganic phosphate disappeared and those of manganous phosphate remained.

Examination of the angles of rotation shows that in every case regardless of compound or valence state the seven minima make their appearance in the same order. The differences in the nicol rotation between the several compounds is due to differences in concentration of the solutions employed.

The isotope which can be observed at the largest nicol rotation is the most abundant and thus corresponds to manganese of atomic mass 55, which is the only one reported by Aston.[4] The three isotopes having a higher scale reading would be lighter and the three having a lower scale reading would be heavier[5] than 55 which would be consistent with an atomic weight of 54.93.

Summary

The magneto-optic method shows that manganese has seven isotopes, of which three are lighter and three heavier than 55, the most abundant one.

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[4] Aston, *Nature*, **112**, 449 (1923).

[5] Bishop, Lawrenz and Dollins, *Phys. Rev.*, [2] **43**, 43 (1933).

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RECEIVED MAY 29, 1933
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[CONTRIBUTION FROM THE ALABAMA EXPERIMENT STATION]

Isotopes of Sodium and Cesium

BY C. B. DOLLINS AND EDNA R. BISHOP

During quantitative studies of calcium by the magneto-optic method,[1] persistent setting on points at which no minima were known, demanded investigation. These minima were more persistent on dilution than those of calcium compounds and, therefore, could not be attributed to another isotope of calcium and so led to a study of the isotopes of sodium and this in turn to those of cesium.

Several investigations[2] by other methods have failed to give evidence of the existence of isotopes of either sodium or cesium and have shown that if isotopes exist they must be present in very small amounts.

The magneto-optic method[3] is well adapted to the study of isotopes that are present in very small amounts, because, due to the mutual influence[4] of isotopes, there is little difference between the concentrations at which the most abundant and the least abundant isotopes produce their characteristic minima.

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[1] Bishop and Dollins, THIS JOURNAL, **54**, 4585 (1932); Bishop, Dollins and Otto, *ibid.*, **55**, 4365 (1933).

[2] Aston, *Phil. Mag.*, **42**, 436 (1921); Aston, *Nature*, **107**, 72 (1921); Bainbridge, *Phys. Rev.*, **36**, 1668 (1930); Bainbridge, *J. Franklin Inst.*, **212**, 317 (1931); Aston, *Proc. Roy. Soc.* (London), **134**, 371 (1932).

[3] Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

[4] Allison, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 9 (1932); *Science*, **77**, 494 (1933).

Experimental

C. p. sodium and cesium salts were dissolved in water freshly redistilled from an all Pyrex still and these solutions were examined by the magneto-optic method. A careful search in the appropriate regions of the scale revealed three minima for the chloride, phosphate, sulfate and nitrate of sodium. Six minima were found for each of the same four compounds of cesium. The presence of three minima for sodium and six for cesium compounds indicates that these elements have three and six isotopes, respectively. The scale readings are shown in Table I.

The greatest nicol rotation[1] at which each minimum could be seen was determined. The results in Table I show that all minima ascribed to each compound became visible at nicol settings which were very close together. Therefore, these minima must either be due to isotopes which become visible in close succession because of mutual influence[4] or to a contamination that has such a weight that it gives minima at these regions of the scale, and is consistently present at approximately the same concentration as the salt studied. The latter is highly improbable in several C. P. salts and, hence, it is concluded the minima are due to isotopes of sodium and cesium.

TABLE I

SCALE READINGS AND NICOL ROTATION OF SODIUM AND CESIUM ISOTOPES IN VARIOUS COMPOUNDS

Order of abundance	Nitrate		Sulfate		Chloride		Phosphate	
	Scale reading	Nicol rotation	Scale reading	Nicol rotation	Scale reading	Nicol rotation	Scale reading	Nicol rotation
				Sodium				
3	7.15	28° 9′	12.83	28° 9′	18.72	28° 9′	23.84	28° 9′
1	7.21	29°59′	12.93	29°59′	18 83	29°59′	24.06	29°59′
2	7.27	29° 2′	13.03	29° 2′	18.92	29° 2′	24.26	29° 2′
				Cesium				
5	10.68	33°51′	26.70	33°51′	39.45	1°53′	50.15	1°53′
4	10.75	34° 9′	26.85	34° 9′	39.54	2° 8′	50.34	2° 8′
1	10.81	34°55′	26.97	34°55′	39.65	2°42′	50.49	2°42′
2	10.85	34°39′	27.06	34°39′	39.76	2°32′	50.68	2°32′
6	10.90	33°51′	27.18	33°51′	39.89	1°36′	50.85	1°36′
3	10.95	34°15′	27.33	34°15′	40.04	2°19′	51.04	2°19′

Water when examined immediately after redistillation from an all Pyrex still showed none of the minima attributed to sodium or cesium compounds. The minima of sodium chloride, however, appeared after the water had stood in the cell for a few minutes.

The nicol rotation determinations also gave the order of abundance of the isotopes. The most abundant isotope produces its minimum at the greatest angle. The great difference in nicol rotation was due to the different concentrations of sodium and cesium salts used in the experiments. In every case the order of appearance of the minima was the same in every compound of the same element. The results are shown in Table I.

The most abundant isotope of sodium must have an atomic mass of 23 as this is the only one detected by Aston[2] and Bainbridge.[2] Since the lightest isotope corresponds to the greatest scale reading,[5] the lightest isotope is the second in abundance and the heaviest the least abundant. Therefore, the atomic weight of sodium would be less than 23. This agrees with the chemically determined value of 22.997. The differences between the circle readings of the sodium minima are abnormally large, which probably indicates that the two least abundant sodium isotopes are present in very minute quantities.

The most abundant cesium isotope must have an atomic mass of 133 as this is the only one previously detected.[2] The isotopes which are second, third, and sixth in order of abundance are lighter than Cs^{133}, whereas the isotopes that are fourth and fifth in order of abundance are heavier than Cs^{133}. Therefore, cesium should have an atomic weight less than 133, which is consistent with the older chemically determined value of 132.81 or with the recent value of 132.91 obtained by Baxter and Thomas[6] or with Aston's value of 132.917.[7]

Summary

The magneto-optic method shows that sodium has three isotopes, one heavier and one lighter than 23, and that cesium has six isotopes, three lighter and two heavier than 133.

(5) Bishop, Lawrenz and Dollins, *Phys. Rev.*, [2] **43**, 43 (1933).

(6) Baxter and Thomas, THIS JOURNAL, **55**, 858–859 (1933).

(7) Aston, *Proc. Roy. Soc.* (London), **134**, 517 (1932).

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

Solubility of Thallous Iodate and Thallous Chloride in the Presence of Amino Acids[1]

BY CRAWFORD F. FAILEY

The view that aliphatic amino acids exist in aqueous solution as molecules each of which bears both a positive and a negative charge has met with increasing acceptance. One question which arises in connection with this theory of ampholytes concerns their effect on the activity coefficients of electrolytes; does log $\gamma_{\pm}$ of a salt vary with the square root of concentration, as if amino acids contributed to the ionic strength, or is their known influence on the dielectric constant of the medium sufficient to account for any changes observed?

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[1] This work was aided by a grant from The Chemical Foundation.

La Mer and Goldman[2] have measured the solubility of thallous iodate in ethyl alcohol–water mixtures, and found that the reasonable value, r = 0.78 Å., for the mean ionic radius satisfies the equation

$$\log_{10} S_1/S_2 = (0.4343/2r)\,\epsilon^2/kT\ \ (1/D_2 - 1/D_1) \qquad (1)$$

where S_1 and S_2 are the solubilities in media of dielectric constant D_1 and D_2, respectively. No measurements of the dielectric constant in dilute alcohol were available to them, but data recently published by Wyman[3] indicate an apparent variation in r of only 30% over the entire solubility range.

Experimental

The preparation and method of analysis of thallous iodate were those of La Mer and Goldman.[4] The thallous chloride used was a C. P. preparation twice recrystallized, and its solubility was determined by gravimetric chloride analyses. Dimethylglycine was prepared by hydrolyzing its ethyl ester (b. p. 148–149°) with sulfuric acid and removing the acid with baryta. β-Alanine was prepared from succinimide by the process of Holm.[5] The remaining substances, recrystallized from commercial material, were all salt free and had the following nitrogen content: glycylglycine 20.90%, glycine 18.70%, α-alanine 15.59%, sarcosine 15.57%, α-

TABLE I

SOLUBILITY OF $TlIO_3$ IN WATER = $S_0 = 1843 \times 10^{-6}$ AT 25°

Solvent,	N =	Soly × 10^6	Solvent,	N =	Soly. × 10^6
Glycylglycine	0.20	2282	α-Amino-n-butyric acid	0.10	1906
				.20	1971
Glycine	0.025	1875	Dimethylglycine	0.025	1859
	.05	1907		.05	1873
	.10	1971		.10	1901
	.15	2033		.20	1957
	.20	2098			
α-Alanine	.025	1872	α-Amino-isobutyric acid	.05	1874
	.05	1907		.10	1901
	.10	1963		.15	1934
	.20	2084		.20	1956
β-Alanine	.025	1863	α-Amino-n-valeric acid	.10	1895
	.05	1884		.20	1939
	.10	1919			
	.15	1964	Urea	.025	1845
	.20	2001		.05	1851
Sarcosine	.05	1880		.10	1861
	.10	1917		.15	1876
	.15	1954		.20	1891
	.20	1993	Diketopiperazine	.10	1844

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(2) V. K. La Mer and F. H. Goldman, THIS JOURNAL, **53**, 473 (1931).

(3) Wyman, *ibid.*, **53**, 3292 (1931).

(4) V. K. La Mer and F. H. Goldman, *ibid.*, **51**, 2632 (1929).

(5) F. H. Holm, *Arch. Pharm.*, **242**, 590 (1904).

amino-*n*-butyric acid 13.72%, α-aminoisobutyric acid 13.56%, α-amino-*n*-valeric acid 11.84%, urea 46.64%, diketopiperazine 24.57%. Samples were rotated overnight in a water thermostat at 25.00 ± 0.01°, it having been shown that the same solubility was observed on approaching equilibrium from a higher temperature. Thallous iodate solubilities are the mean of duplicate analyses, the average difference between duplicates being 0.16%. In a series of twelve independent determinations of the water solubility the greatest difference between any two measurements was 0.3%. All concentrations are expressed as moles per liter.

Discussion

The results with thallous iodate are given in Table I. They are plotted in Fig. 1 with log S/S_0 as ordinate and amino acid concentration as abscissa, S_0 being the solubility in water.

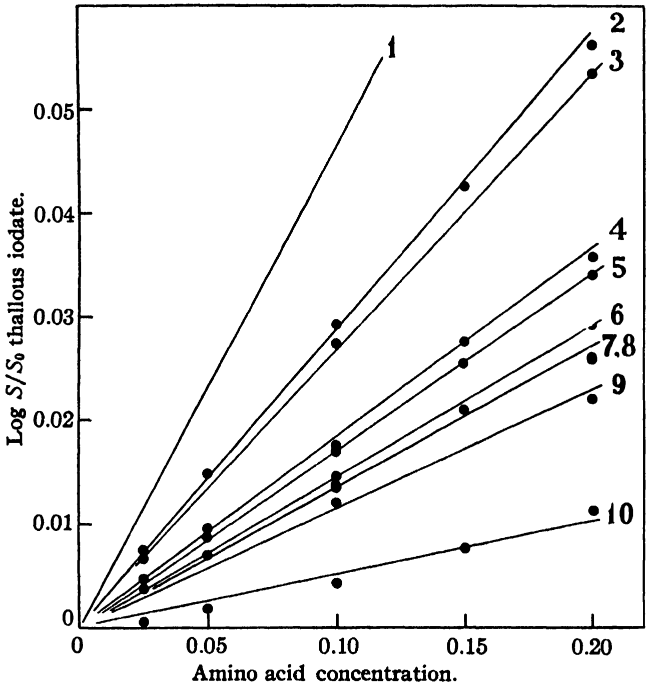

Fig. 1.—1, Glycylglycine; 2, glycine; 3, β-alanine; 4, α-alanine; 5, sarcosine; 6, α-amino-*n*-butyric acid; 7, dimethylglycine; 8, α-aminoisobutyric acid; 9, α-amino-*n*-valeric acid; 10, urea.

It may be seen that log S/S_0 for thallous iodate is approximately a linear function of amino acid concentration. From the dielectric constant measurements of Wyman and McMeekin[6] one may calculate the following values for *r* in equation 1: in the presence of glycine 1.49 Å., β-alanine

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(6) J. Wyman, Jr., and T. L. McMeekin, THIS JOURNAL, 55, 908 (1933).

2.36 Å., α-alanine 2.43 Å., glycylglycine 2.56 Å., α-amino-*n*-butyric acid 2.98 Å., and α-amino-*n*-valeric acid 3.83 Å. Although these radii are of the right order of magnitude, their differences indicate that the simple theory is inadequate. For example, all four normal α-amino acids have nearly the same effect on the dielectric constant of water and should, mole for mole, change the solubility of a salt equally. Diketopiperazine, which according to Devoto[7] decreases slightly the dielectric constant of water, is found to be without solvent action. Since log solubility is a linear function of amino acid concentration and not of its square root, the interaction is of a different character from that between strong electrolytes.

Glycine and its three N-methyl derivatives form an interesting series, the solvent action decreasing with increasing molecular weight. Again it may be observed that the isomers alanine and sarcosine have almost the same effect, likewise dimethylglycine, α-amino-isobutyric acid and α-amino-*n*-butyric acid. The separation of the positive and negative groups in going from α- to β-alanine which enhances the effect on the dielectric constant of water is accompanied by an increased dissolving power.

A test of equation 1 independent of dielectric constant measurements may be applied by considering the solubilities of two different salts in the same aqueous solvent. In this case we should find that a constant K satisfies the following equation and is independent of the solvent.

$$(\log S_{1A}/S_{0A})/(\log S_{1B}/S_{0B}) = r_B/r_A = K \qquad (2)$$

where S_{1A} is the solubility of salt A in solvent 1, S_{0A} its solubility in water, and r_A its mean radius.

In Table II are given some solubilities of thallous chloride in amino acid solutions. The last column, which shows the value of K in equation 2, indicates that, while it is not strictly constant, the variations are not wide.

TABLE II

SOLUBILITY TlCl IN WATER = S_0 = 1611 × 10^{-5} AT 25°

Solvent		Soly. TlCl × 10^5	K
Glycylglycine, $N = 0.2$		1835	1.64
Glycine, $N = 0.2$		1725	1.91
α-Alanine, $N = 0.2$		1703	1.49
α-Amino-*n*-butyric acid,	$N = 0.1$	1648	1.46
	$N = 0.2$	1688	1.45
α-Amino-isobutyric acid,	$N = 0.2$	1679	1.45
α-Amino-*n*-valeric acid,	$N = 0.1$	1627	2.82
	$N = 0.2$	1633	3.75
Urea, $N = 0.2$		1642	1.81
Diketopiperazine, $N = 0.1$		1604	

Summary

The solubilities of thallous iodate and thallous chloride in the presence of amino acids have been determined. The logarithm of thallous iodate

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[7] G. Devoto, *Gazz. chim. ital.*, **61**, 897 (1932).

solubility is approximately a linear function of the concentration of added substance. The dielectric constants of the solutions do not account for differences observed between the α-amino acids but permit the calculation of ionic radii for the salts which are of the right order of magnitude.

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Low Temperature Specific Heats. I. An Improved Calorimeter for Use from 14 to 300°K. The Heat Capacity and Entropy of Naphthalene[1]

BY J. C. SOUTHARD AND F. G. BRICKWEDDE

The calorimeter described in this paper has been constructed for the determination of the specific heats of liquids and solids of interest in fertilizer and nitrogen fixation investigations. Slow thermal changes anticipated in some of the substances to be investigated made it desirable to prevent as far as possible any transfer of heat between the substances and the surroundings.

Systematic and reliable low temperature specific heat determinations date from the design of the "vacuum" calorimeter first used by Eucken[2] in Nernst's laboratory, 1909. In principle the specific heat of a substance is determined by observing the rise in temperature produced when a measured amount of heat is added electrically to the substance suspended, for purposes of thermal insulation, in an evacuated space. The "vacuum" calorimeter was modified and improved by later investigators. The apparatus described here is a refinement of a "vacuum" calorimeter used by F. Lange[3] which was the first intended to operate "adiabatically," that is, so there should be no transfer of heat between the substance and its surroundings. This is accomplished by surrounding the substance, in a thin-walled container, with a "thermal" shield whose temperature can be

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(1) This paper is the first of a series communicating the results of two years of coöperative work by the Fixed Nitrogen Research Laboratory and the Bureau of Standards on the specific heats of compounds important in connection with fertilizer and fixed nitrogen investigations of the former laboratory. The experimental work was carried out in the Cryogenic Laboratory of the Bureau of Standards.

The series will include five papers, which with the exception of III will appear in THIS JOURNAL. Number III has already been published in the *Journal of Chemical Physics*, **1**, 95 (1933). The sub-titles of this series for which the principal title is "Low Temperature Specific Heats" are as follows: I. An Improved Calorimeter for use from 14 to 300°K. The Heat Capacity and Entropy of Naphthalene. II. The Calibration of the Thermometer and the Resistance of Pt, Pt-10% Rh and Constantan between −259 and −190°. III. Molecular Rotation in Crystalline Primary Normal Amylammonium Chloride. IV. The Heat Capacities of Potassium Chloride, Potassium Nitrate and Sodium Nitrate. V. The Heat Capacities of β- and α-Tricalcium Phosphate. Publication approved by Director of Bureau of Standards, Department of Commerce, and Chief, Bureau of Chemistry and Soils, Department of Agriculture.

(2) Eucken, *Physik. Z.*, **10**, 586 (1909).

(3) Lange, *Z. physik. Chem.*, **110A**, 343 (1924).

varied quickly and thus made to follow the temperature changes of the surface of the container. An adiabatic calorimeter with such a shield was used by Southard and Andrews for the determination of specific heats at low temperatures.[4] Under ideal conditions there would be no difference in temperature between the container and any part of the shield, and the substance in its container would neither lose heat to its surroundings nor gain heat from them.

Apparatus

The apparatus described here may be considered as being composed of four principal parts, (1) the inner container in which the material under investigation is placed, (2) the thermal shield surrounding the inner container, used to minimize heat leaks, (3) the jacket, inclosing the inner container and thermal shield, connected to a high vacuum system for evacuation to minimize gaseous conduction and convection of heat, and (4) the various electrical circuits for determining and controlling the temperature and for measuring the energy added to the inner container.

The inner container (Fig. 1A) is a cylindrical copper can (5 × 4 cm.) fitted with a reentrant tube (4.5 × 0.5 cm.) in which is soldered the platinum case of a specially constructed resistance thermometer which also serves as the heater. Around the tube are sixteen radial fins of 0.1 mm. copper foil. The top, which can be unsoldered and removed for loading, is pierced by a pin hole through which helium is admitted just before the final vacuum tight sealing. A small screw is soldered to the side of the container for attaching one junction of a difference thermocouple pressed into contact by a nut. The other junction is attached to the middle of the inside cylindrical surface of the thermal shield. The outside of the inner container is silver plated to reduce the transfer of heat to and from the container by radiation. The empty container has a weight of about 37 g., including the resistance thermometer, an inside volume of 54 cc., and a heat capacity of approximately 3 cal./degree at room temperature.

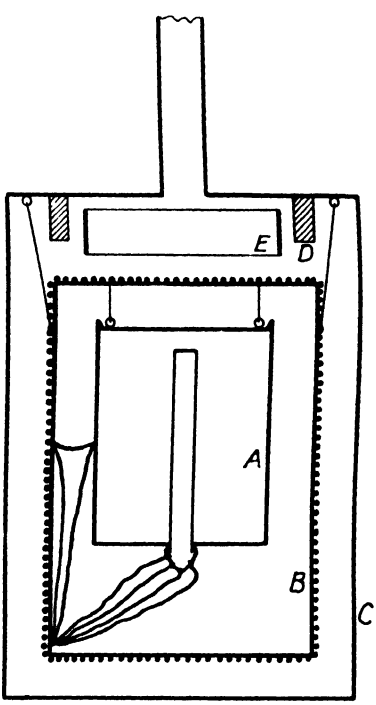

Fig. 1.—Calorimeter for low temperature specific heats: A, inner container; B, thermal shield; C, jacket; D, ring on top; E, floating ring.

The thermal shield (Fig. 1B) completely surrounds the inner container which is suspended inside of it on silk threads. The shield is a cylindrical brass shell (6 × 8.5 cm., wall thickness 0.8 mm.) fitted with a removable bottom. Its inside surface is gold plated and the outside completely covered by three separate heaters, one each on the top, side and bottom, made by covering the surface with a single layer of No. 32 constantan wire insulated with silk and bakelite lacquer. The electrical leads to the heater-thermometer and to three copper-constantan difference thermocouples are run under the heater winding, in a spiral groove, 75 cm. long, cut in the side of the shield. One of the thermocouples is that previously referred to, between the inner container and side of the shield. The other two are between the inside top and side, and the inside bottom and side of the shield. Their e. m. f.'s, as indicated by a sensitive d'Arsonval type galvanometer, serve as a guide for the regulation of the shield heaters. In order to prevent a cold spot where the leads enter the groove, it was found necessary to wind the leads around a floating ring (E) whose temperature was kept within a few degrees of that of the shield by means of an auxiliary heater and difference thermocouple.

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[4] Southard and Andrews, *J. Franklin Inst.*, **209**, 349 (1930).

The jacket (Fig. 1C) is a brass case made in two separable parts, surrounding the shield. The lower part can be removed by unsoldering a slip joint at the outer edge of the top. The space inside the jacket is connected to a high vacuum system by a thin walled copper–nickel alloy tube (o. d. 1 cm.) through which the electrical leads pass. On the inside of the top is soldered a heavy copper ring (D) around which the leads, coming from warmer regions above, are wound in order to bring them to the temperature of the surrounding bath. Without the ring, the inner container could not be maintained at a temperature as low as that of the bath. The jacket is surrounded by a refrigerating bath in a Dewar flask, enclosed in a vacuum tight case connected to a high capacity mechanical vacuum pump. Using liquid air or liquid hydrogen, temperatures can be maintained with this pump corresponding to vapor pressures of 3 cm. A larger Dewar flask filled with liquid air is placed outside the case of the inner flask when the latter contains liquid hydrogen.

The combination thermometer-heater was made of an alloy, platinum–10% rhodium wire and has a resistance of about 53 ohms at 273°K. Its construction and its calibration below 90°K. against a gas thermometer are described in another paper[5] in which it is designated as K_4. Above 90°K. it was calibrated by comparison with a standard platinum resistance thermometer in a precision cryostat.[6] The equation $R/R_0 = 1 + at + bt^2 + ct^3$, in which the temperature is expressed in °C. (International) and $a = +0.00172075$, $b = -2.28297 \times 10^{-7}$, $c = -1.77572 \times 10^{-9}$ was found to represent the data with a maximum deviation of 0.006°. When the thermometer-heater was used as a thermometer its resistance was ascertained by determining the ratio of the potential drop across its ends to that across a standard 100-ohm coil connected in series, when a current of 1 ma. is flowing through them. When the thermometer was used as a heater the current and voltage were measured potentiometrically using a 1-ohm standard resistor and a 10,000-ohm volt box. The time of heating is controlled by an automatic switch operated by the standard time signals of the Bureau of Standards. Lead storage batteries of 120 volts are the source of heating current.

The three shield heaters each have a slide wire rheostat in series for independent regulation. In addition there is a master rheostat controlling all three circuits as a unit. The floating ring heater is independent of the shield. As an aid to regulation and for protection, a milliammeter and a 250 ma. fuse are connected in each of these circuits.

Two observers are needed. One makes a series of ten or more determinations at one-minute intervals of the thermometer resistance by comparing the potential across it with that across the standard resistance in series with it. After these measurements, during the following silent or fifty-ninth second of the time signals, the activating circuit of the automatic switch is closed so that the next time signal impulse throws the switch and begins the heating period. The current which flows through the heater in the inner container when the switch is thrown has previously been flowing through a steadying resistance so that the load on the batteries is constant. During the heating period of from five to ten minutes not less than four readings each on volt box and standard resistor are made. During these observations the other observer has been regulating the

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(5) Southard and Milner, THIS JOURNAL, 55, 4384 (1933).

(6) Scott and Brickwedde, *B. of S. J. Res.*, 6, 401 (1931).

shield heaters, top, side and bottom, so that the temperature of all parts of the shield as shown by the difference couples connected one after another to a galvanometer has closely followed that of the calorimeter. The automatic switch is reversed so that after the required number of minutes of heating the heating current is automatically switched to the steadying resistances by closing the activating switch as was done on starting. After a period of three or four minutes, when equilibrium is established, another series of thermometer resistance measurements is made and the procedure continued.

The temperature difference between shield and calorimeter is kept within 0.02°, with the exception of short intervals at the beginning and the end of the heating period, when it may rise to 0.05°. With a thermal head of 0.02° it was found that the temperature of the inner container did not change by as much as 0.001° during half an hour. This feature makes the calorimeter well suited for the investigation of slow thermal transitions since with such constancy a small amount of energy evolved or absorbed over a long period of time can be measured with accuracy.[7] Although in practice a liquid bath is used whose temperature does not differ much from that of the inner container, it was found that measurements made at 0° with a liquid air bath surrounding the jacket were as reliable as those made with a cool acetone bath at −10°. Measurements taken in the same temperature range on different days using refrigerating baths of widely differing temperatures were in agreement with each other within the limits of accuracy given in this paper.

Halving the rate of heating yields results which are in agreement with each other and with those found with the original rate of heating. Thus it is made apparent that the net transfer of heat to or from the inner container by radiation and by conduction along leads is negligibly small.

The principal source of error is in the measurement of the temperature rise. An error of 0.002° in the determination of a temperature rise of about five degrees makes for an error in heat capacity of 0.04%. The potentiometer with which the temperature and energy input determinations were made was periodically calibrated. Down to −190° temperatures are probably correct to within 0.01° on the International Temperature Scale and it is believed to within 0.05° on the thermodynamic scale between −190 and −250°, in which region the thermometer was calibrated against a gas thermometer. Temperature changes were determined with an accuracy of 0.002° down to −230°. Because of the uncertainty in the value of the thermodynamic temperature of the ice point, here taken as 273.16°, absolute temperatures may be in error by 0.05°K. Oscillograph measurements showed that the lag in the automatic heating circuit switch did not contribute errors exceeding 0.01 second. Irregularities in the time signals might account for an additional 0.02 second, which, however, in a heating period of three hundred seconds is negligible.

The correction for the irregularity in energy input while the heater resistance is rising to a steady state at the beginning of a run does not amount to more than 0.1% of the energy input. The actual error introduced, however, is only a fraction of this. The correction is calculated from a series of readings made at fifteen-second intervals during the first minute. It was found that such a series need only be taken occasionally and especially when the heating current was changed. Another correction of about 0.1% is required on account of the heat generated in the leads passing between the shield and the inner container. The heat generated is calculated from direct measurements of the lead resistance made during each heating period. On the assumption that this heat divides equally between the shield and the inner container, the error in applying the correction is very small. Measurements of electric power input are probably accurate to about 0.02%. The experimental error in determining the heat capacity of the

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(7) This calorimeter was used in the investigation of the slow thermal changes which take place in primary amylammonium chloride, *J. Chem. Physics*, **1**, 95 (1933).

empty calorimeter may introduce an error of 0.02 to 0.03% in the final results of a heat capacity determination.

The errors from all sources total about 0.1%. Plotting the data, the precision of measurement appears to be about this magnitude down as far as 40°K. Below this temperature the errors increase because of the decreasing sensitivity of the thermometer, and the increasing ratio of the heat capacity of the empty inner container to that of the sample. At the lower temperatures the thermal conductivity of the leads increases rapidly. At temperatures therefore for which the energy input is smallest there may be appreciable transfers of heat to or from the inner container. It is possible that at 14°K. the errors may in the worst cases exceed 1%.

Results

Naphthalene was selected for investigation for two reasons. (1) It is a good substance for testing the accuracy of the results obtainable with the calorimeter since it has been used by a number of other workers[8] and (2) because use has been made of it as a standard in calibrating other types of low temperature calorimeters.[9] It is obtainable from the Bureau of Standards as a standard sample[10] in a sufficient degree of purity to be used without further treatment.

In these measurements the international joule is used as the unit of energy, so that the specific heats are obtained in joules per gram degree. Except for the fact that the results of most of the other measurements have been expressed in calories, it would be desirable to give these results in international joules as they were obtained. For convenience of comparison with other results, the calorie has been used. The "I. C. T." defines the calorie as follows: 1 g. cal._{15} = 4.185 abs. joule. The factor relating the absolute joule and the Bureau of Standards international joule is, according to the latest information,[11] 1 int. joule = 1.0004 abs. joule, so that 1 g. cal._{15} = 4.185/1.0004 = 4.1833 int. joules. All weights are corrected to vacuum.

The results are presented in Table I and Fig. 2. The entropy at 298.16°K. was found to be 39.89 ± 0.12 e. u. by plotting C_p/T against T and measuring the area under the curve. This involved an extrapolation of 0.43 e. u. for the portion below 15°K. Six degrees of freedom for each of which θ_D was set equal to 133 were used to obtain this extrapolated value. Taking the entropy of C as 1.39 e. u. per mole[12] and H_2, 31.23 e. u.[13] at 298.16°K., and the heat of combustion of naphthalene as 1,231.6 kg. cal.[14] per mole, hydrogen 68.31 kg. cal.[15] and carbon 94.24 kg. cal.,[16]

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(8) Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1555 (1930); Andrews, Lynn and Johnston, *ibid.*, **48**, 1274 (1926); Taylor and Rinkenbach, *ibid.*, **46**, 1504 (1924); Dewar, *Proc. Roy. Soc.* (London), **76A**, 325 (1905).

(9) Smith, THIS JOURNAL, **53**, 3663 (1931).

(10) Standard sample 38b (naphthalene) is purified by two crystallizations from alcohol and sublimation in vacuum (see Bureau of Standards Circ. 25).

(11) Vinal, *Bur. Standards J. Research*, **8**, 448 (1932).

(12) "I. C. T.," Vol. V, p. 87.

(13) Giauque, THIS JOURNAL, **52**, 4816 (1930).

(14) "I. C. T.," Vol. V, p. 163.

(15) Rossini, *Bur. Stds. J. Res.*, **6**, 1 (1931).

(16) Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925).

TABLE I

MOLAL HEAT CAPACITY OF NAPHTHALENE

Mol. wt. 128.06. 273.16°K. = 0°C. Wt. sample (*in vacuo*), 37.121 g. C_p in 15° calories per mole.

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
15.14	1.411	62.32	10.52	140.33	18.46	218.13	27.86
17.73	2.035	62.52	10.54	145.61	19.04	223.10	28.52
21.45	2.964	67.86	11.10	150.80	19.67	226.90	29.09
22.25	3.283	73.36	11.69	151.99	19.77	228.01	29.25
25.54	4.058	78.58	12.26	155.93	20.20	232.92	29.87
26.66	4.337	83.57	12.92	161.02	20.79	232.95	29.84
29.79	5.074	88.38	13.29	163.48	21.03	237.78	30.45
31.74	5.507	89.86	13.44	166.00	21.34	238.94	30.66
34.35	6.068	93.06	13.72	168.52	21.54	242.54	31.28
36.47	6.513	95.39	13.86	173.49	22.16	244.83	31.57
39.34	7.038	100.77	14.46	178.39	22.74	250.68	32.39
41.32	7.395	106.04	14.86	183.23	23.36	256.42	33.23
44.64	7.916	111.18	15.38	187.99	23.94	262.09	34.11
46.53	8.222	116.21	15.85	192.69	24.65	267.70	34.98
50.23	8.730	121.11	16.35	197.62	25.17	273.21	35.86
51.95	9.071	125.94	16.93	202.85	25.84	278.69	36.76
56.22	9.709	130.68	17.43	208.00	26.52	284.09	37.65
57.37	9.878	135.35	17.93	213.10	27.19	289.42	38.54
						294.68	39.55

at the same temperature, the free energy of formation of naphthalene at 298.16°K. is found to be +48.5 kg. cal. per mole.

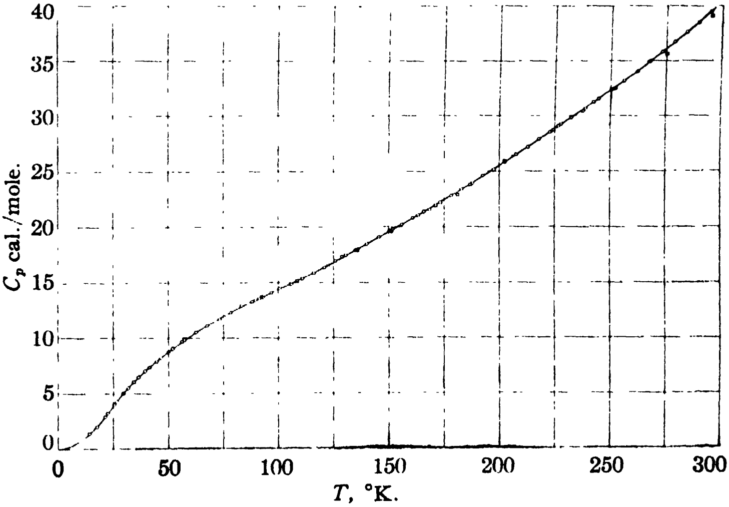

Fig. 2.—Molal heat capacity of naphthalene, $C_{10}H_8$: ○, S. and B.; □, H., P. and D.; ▽, T. and R.

The heat capacities of naphthalene reported in Table I, determined with the apparatus described, agree with the heat capacities determined by

Huffman, Parks and Daniels between 90 and 300°K. well within the limits of accuracy claimed by them (1%). Furthermore, there is no tendency for one curve to be consistently higher or lower than the other up to 250°K. It should be pointed out while Huffman, Parks and Daniels used a "vacuum" calorimeter, their method of operation was entirely different and it seems probable that their corrections for radiation lead to the divergence at the higher temperatures.

It is interesting to note that the value Huffman, Parks and Daniels obtained by extrapolation from 90 to 0°K. for the entropy at 90°K. was 12.69 e. u. while the value found here is 12.52 e. u. with an extrapolation of only 0.43 e. u. from 15 to 0°K.

Acknowledgment.—The authors are indebted to Dr. R. T. Milner for his helpful suggestions in the construction of the apparatus and for his assistance in measurements on the empty calorimeter. They are indebted to Mr. J. W. Cook for liquefying the hydrogen and to Mr. R. A. Nelson for assisting in the measurements and calculations on naphthalene.

Summary

1. An improved adiabatic calorimeter for the measurement of specific heats of liquids and solids between 14 and 300°K. has been constructed. It can be used with a precision of about 0.1% and is particularly suited to the study of slow transitions and thermal changes.

2. The molal heat capacity of naphthalene was determined between 14 and 300°K. and the entropy and free energy of formation at 298.16°K. calculated to be 39.89 ± 0.12 e. u. and +48.5 kg. cal., respectively.

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Low Temperature Specific Heats. II. The Calibration of the Thermometer and the Resistance of Platinum, Platinum–10% Rhodium and Constantan between –259 and –190°

BY J. C. SOUTHARD AND R. T. MILNER

In the determination of a thermal property, the temperature scale and the thermometer that are used are of such fundamental importance that they deserve special consideration. The International Temperature Scale[1] was used for the specific heat measurements described in this series in the range over which it is defined, that is, above –190°. Below this temperature there is no accepted or established scale except that obtained by the use of a gas thermometer. This paper describes a helium constant volume thermometer that was used in a relatively simple manner to obtain a knowledge of the resistance of specimens of platinum, platinum–10% rhodium and constantan at temperatures below −190°.

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[1] G. K. Burgess, *Bur. Standards J. Research*, 1, 635 (1928).

The resistance of platinum down to −259° has been measured at Leiden[2] and at the Reichsanstalt,[3] by comparison with gas thermometers. The relation between resistance and temperature below −190° is of a complex nature and up to this time has not been represented by an equation containing only a few constants. Simple deviation formulas to account for differences between various samples of platinum have been proposed[4] but there have been no detailed comparisons with experiment. Since the standard platinum resistance thermometer is used from −190 to 660°, it would be desirable to use this same metal below −190° if possible. Others have used copper–constantan thermocouples[5] and lead resistance thermometers. The latter were calibrated[6] by comparison with a platinum thermometer.

Apparatus

The gas thermometer bulb of 20 cc. capacity is formed by a very heavy-walled, cylindrical copper container (5 × 5.5 cm., wt. 760 g.). The inner surface of the bulb was machined smooth but not polished. The platinum cases of the resistance thermometers were soldered in holes in the heavy wall of the bulb. The bulb is connected to a manometer by a capillary tube (0.27 mm. i. d.) one meter long, made of a copper–nickel alloy of low thermal conductivity. The copper container is surrounded by a thermostated shield which can be so controlled that its temperature will not change 0.001° during periods of over half an hour.[7] All leads to the thermometers enter through a spiral groove in the shield. The capillary which passes through the outer bath which is below the temperature of the bulb has on it a separate difference thermocouple and heater which can be controlled so that the temperature gradient in the portion of the capillary next to the bulb is negligible. The bulb and shield are suspended in an evacuated brass jacket which is immersed in liquid hydrogen or liquid air. The liquid bath is enclosed by another jacket to which a vacuum pump may be attached.

The resistance thermometers are of a so-called "strain-free" four lead type, recently developed at the Bureau of Standards.[8] Wire of about 0.1 mm. diameter is wound into an open helix of approximately 0.5 mm. outside diameter which in turn is wound around a notched mica cross. After annealing the wire on the cross, the thermometer is slipped into a snug fitting cylindrical platinum case (5 × 45 mm.). The leads are brought out through a soft glass cap on the open end in such a manner that they are insulated from each other. After the case has been evacuated and filled with helium to about one-third atmosphere, the glass cap is sealed off close to the case. Two pure platinum thermometers (K_2 and K_V), a platinum–10% rhodium thermometer (K_4) and a constantan thermometer (K_5) were so constructed. K_V and K_5 were wound on the same mica cross and placed in a single tube together. The resistances of the ther-

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(2) Cath, Onnes and Burger, *Comm. Phys. Lab. Univ. Leiden* 52 c, 1917; "I. C. T.," Vol. VI, p. 130. See also *Communications Phys. Lab. Univ. Leiden* Suppl. 58 (1926).

(3) Henning and Otto, *Z. ges. Kälte-Ind.*, **39**, 86 (1932).

(4) Nernst, *Sitz. preuss. Akad. Wiss. Physik-math. Klasse* 311 (1911); Henning, *Naturwissenschaften*, **16**, 617 (1928).

(5) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

(6) Clusius and Vaughen, *Z. ges. Kälte-Ind.*, **36**, 215 (1929).

(7) Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).

(8) C. H. Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).

mometers are measured by comparison with a 100-ohm standard coil by means of a White double potentiometer and a type H. S. Leeds and Northrup galvanometer. Both the 100-ohm coil and the potentiometer had been calibrated by the electrical resistance section of the Bureau of Standards less than a week before use.

The U-type manometer was constructed from selected Pyrex tubing (10 mm. i. d.) of very uniform bore. The metal capillary was connected to one limb through a brass plug bearing a platinum pointer 1 mm. long to which the mercury meniscus was adjusted by means of a leveling bulb mounted on a traveling screw device. The other limb of the manometer was connected to a high vacuum system. The height of the column was read on a mirror-back calibrated glass scale to about 0.1 mm. with the unaided eye. As shown in the discussion later this precision of reading was ample.

Procedure

The copper bulb was first cooled to liquid air temperatures, helium admitted to a pressure of about one atmosphere, and the manometer filled with mercury through the leveling bulb. The helium had been purified by passing it first through activated charcoal immersed in liquid air and then through a spiral filled with charcoal immersed in liquid hydrogen.

The apparatus was then cooled to the triple point of hydrogen, the jacket evacuated to a pressure of less than 10^{-5} mm., and the shield regulated to maintain its temperature constant. A series of five resistance measurements was made on each thermometer while a number of manometer readings were being taken. During the time required for these readings the temperature of the bulb did not change by an amount detectable with either the manometer or the resistance thermometers. The block and shield were then heated from two to five degrees and the above procedure repeated.

Discussion of Results

In this type of gas thermometer there are three interconnected volumes which may be considered as being at three different temperatures.[9] If the temperature of each of these is considered uniform, and if the gas is assumed to obey the law pv/T = constant, then

$$p\left(\frac{V}{T_v} + \frac{v_m}{T_m} + \frac{v_c}{T_c}\right) = C \qquad (1)$$

where p is the pressure, V the volume of the bulb of the gas thermometer, v_m the volume in the manometer, v_c the volume of the capillary, T_v, T_m and T_c the temperatures of these respective volumes, and C depends on the total mass of gas. Here T_c represents the average or effective temperature of the capillary. If V is expressed as a function of temperature, $V = V_0(1 + \alpha\ (T_v - T_0))$ where V_0 is the volume at any reference temperature T_0, and α is the coefficient of expansion of copper, equation (1) becomes

$$T_v = \frac{pV_0}{C}\left[1 + \alpha\ (T_v - T_0) + \frac{v_m T_v}{V_0 T_m} + \frac{v_c T_v}{V_0 T_c}\right] \qquad (2)$$

as a sufficient approximation between 90 and 14°K. where α is 6.28×10^{-5}. Although T_v occurs on both sides of this equation, it is found on the right only in "correction" terms, so that successive approximations give T_v to any desired exactness. V_0/C is a constant which may be determined from

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(9) For a more complete discussion see Henning, "Hand. d. Physik," Verlag Julius Springer, Berlin, 1926, Vol. IX, p. 532.

measurements at any reference temperature where T_v may be taken by definition. In this case the boiling point of oxygen was selected as the reference temperature and T_v obtained from the observations on thermometers K_2 and K_v which had been calibrated previously against an oxygen vapor pressure thermometer in a bath of boiling oxygen. The normal boiling point of oxygen is $-182.97°$ on the international temperature scale and with 273.16°K. for the ice point, this is 90.19°K.

With an initial pressure of 1 atmosphere at 90°K., a precision of 0.1 to 0.2 mm. in the manometer readings is equivalent to 0.01 or 0.02° in T_v. The calculation of the change of volume of the bulb with temperature is entirely dependent on measurements made at Leiden,[10] which appear to be uncertain by a factor of 1×10^{-4} at the lowest temperatures. The equation $V = V_{90}(1 + 6.28 \times 10^{-5}(T-90))$ was found to fit the data for copper satisfactorily below 90°K. Corrections for the manometer and capillary spaces appear in equation (2) as $v_m T_v/V_0 T_m$ and $v_c T_v/V_0 T_c$. Since $v_m/V_0 = 0.0073 \pm 0.0002$ and $T_v/T_m < 0.3$, uncertainties in the manometer space correction are negligible. Although v_c/V_0 is small (1.1×10^{-3}), the uncertainty in the mean temperature of the capillary T_c is such that an error of 0.01° in T_v may result from the capillary space correction.

Errors in resistance measurements were of the order of 10^{-4} ohm, involving an uncertainty of less than 0.01° in T_v in most cases. The reduction of values of T_v obtained from Eq. (2), which assumes a perfect gas, to the thermodynamic temperature scale was made using the data given by Henning,[11] which according to him are exact to a few thousandths of a degree for a pressure of one meter at 0°. Since the pressure used was equivalent to 2.4 meters at 0°, this uncertainty may amount to 0.01°.

Mendelssohn[12] has used a thermometer similar to this one for measurements at helium temperatures. He could not detect the Knudson[13] thermal pressure gradient when using capillaries of only 0.1 to 0.15 mm. diameter.

The results of the measurements are presented in Table I. A plot of these data would be too small to show deviations of observed values from a smooth curve and the complexity of the curve. Instead, a table of R/R_0 for platinum (K_2) has been constructed (Table II) by fitting two simple cubic equations over different parts of the range, plotting deviations from these and adding the two values algebraically. Figure 1 shows the differences between tabular and observed values. For K_2 the deviation from the axis gives an estimate of the precision while for K_v, with an R/R_0 curve differing from K_2, the deviation from a smooth curve is the criterion. A tabulation for the constantan thermometer K_5 covering the narrow range 14 to 26°K. in which it seems most useful is also given (Table II) and the resistance temperature curve shown in Fig. 2. A table similar to that of K_2 has been constructed for K_4 and the deviations are found to be of the same magnitude.

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[10] Keesom and Van Agr, *Leiden Comm.*, No. 182A.

[11] Henning, *Z. ges. Kälte-Ind.*, **37**, 169 (1930).

[12] Mendelssohn, *Z. Physik*, **73**, 482 (1931).

[13] Knudson, *Ann. Physik*, **31**, 205, 633 (1910); **33**, 1435 (1910).

TABLE I

OBSERVED VALUES OF R/R_0 OF PLATINUM, PLATINUM–10% RHODIUM AND CONSTANTAN FROM 14.44 TO 97.06°K.

0°C. = 273.16°K.

Gas thermometer		R/R_0 K_2	R/R_0 K_4	R/R_0 K_V	R/R_0 K_3
$P_{\text{corr.}}$, cm.	T, °K.	Platinum R_0 = 24.8262 ohms	Pt–10% Rh R_0 = 53.4330 ohms	Platinum R_0 = 19.2149 ohms	Constantan R_0 = 94.6220 ohms
12.46	14.44	0.003529	0.552698	0.003949	0.968158
14.85	17.20	.004664	.553280	.005100	.970853
15.82	18.33	.005289	.553615	.005736	.971944
17.09	19.77	.006255	.554144	.006726	.973320
18.71	21.65	.007786	.554979	.008276	.974934
21.56	24.95	.011415	.556935	.011951	.977324
25.47	29.47	.018412	.560620	.018985	.979570
29.55	34.20	.028422	.565712	.029019	.981046
33.79	39.10	.041315	.572068	.041956	.982313
37.92	43.89	.056166	.579234	.056852	.983431
42.17	48.83	.073285	.587287	.073906	.984440
46.54	53.91	.092334	.596183	.092969	.985468
50.81	58.88	.111995	.605288	.112631	.986453
55.04	63.81	.132320	.614655	.132980	.987432
17.60	20.36	.006707	.554388	.007177	.973852
23.28	26.94	.014201	.558423	.014751	.978390
27.26	31.54	.022492	.562731	.023065	.980222
31.67	36.65	.034580	.568774	.035181	.981713
35.74	41.37	.048191	.575397	.048816	.982858
39.88	46.17	.063864	.582869	.064466	.983905
44.28	51.29	.082425	.591583	.083061	.984959
48.35	56.01	.100599	.600033	.101229	.985904
52.64	61.00	.120848	.609379	.121489	.986900
77.77	90.32[a]	.246195	.666828	.246850	.992395
56.33	65.32	.138833	.617649	.139480	.987744
60.70	70.41	.160431	.627567	.161062	.988737
65.17	75.62	.182642	.637757	.183269	.989730
69.50	80.69	.204522	.647779	.205169	.990680
73.61	85.50	.225230	.657257	.225877	.991549
77.62	90.19[a]	.245635	.666570	.246267	.992376
72.78	84.61	.221540	.655563	.222182	.991383
77.66	90.33[a]	.24632	.666880	.246964	.992379
80.60	93.77	.26111	.673642	.261749	.992973
83.40	97.06	.27537	.680153	.276025	.993525

[a] Calibration point.

To check the accuracy of the gas thermometer measurements the temperature of liquid hydrogen boiling under atmospheric pressure was determined. This was accomplished by admitting helium to the surrounding jacket and allowing the thermometers to come to equilibrium in a bath of liquid hydrogen. The vapor pressure of the bath was determined by reading the barometer, since the pressure coefficient near the boiling point is about 230 mm./degree and even an error of 1 mm. could be neglected. At 750 mm. pressure the helium thermometer gave a temperature of

TABLE II

RESISTANCE OF PLATINUM (FROM 14 TO 109°K.) AND CONSTANTAN (FROM 14 TO 25°K.) AT ONE-DEGREE INTERVALS. READ FROM SMOOTHED DEVIATION CURVES

0°C. = 273.16°K.

T, °K.	R/R_0	*T*, °K.	R/R_0	*T*, °K.	R/R_0
Platinum Thermometer K_2. R_0 = 24.8262 ohms					
14	0.003400	46	0.063288	78	0.193032
15	.003724	47	.066774	79	.197341
16	.004110	48	.070323	80	.201652
17	.004566	49	.073931	81	.205965
18	.005099	50	.077594	82	.210279
19	.005716	51	.081309	83	.214594
20	.006423	52	.085073	84	.218910
21	.007226	53	.088883	85	.223227
22	.008130	54	.092747	86	.227545
23	.009140	55	.096643	87	.231864
24	.010260	56	.100579	88	.236184
25	.011493	57	.104552	89	.240505
26	.012842	58	.108560	90	.244826
27	.014309	59	.112601	91	.249147
28	.015896	60	.116673	92	.253468
29	.017604	61	.120774	93	.257789
30	.019432	62	.124902	94	.262110
31	.021379	63	.129055	95	.266431
32	.023444	64	.133231	96	.270751
33	.025625	65	.137428	97	.275071
34	.027920	66	.141644	98	.279390
35	.030326	67	.145877	99	.283708
36	.032841	68	.150125	100	.288014
37	.035464	69	.154386	101	.292328
38	.038190	70	.158658	102	.296639
39	.041016	71	.162939	103	.300947
40	.043939	72	.167227	104	.305251
41	.046955	73	.171520	105	.309551
42	.050060	74	.175817	106	.313846
43	.053250	75	.180117	107	.318136
44	.056521	76	.184420	108	.322421
45	.059869	77	.188725	109	.326701
Constantan Thermometer, K_5. R_0 = 94.6220 ohms					
14	0.967710	18	0.971654	22	0.975234
15	.968701	19	.972610	23	.976002
16	.969692	20	.973532	24	.976710
17	.970678	21	.974409	25	.977355
				26	.977924

20.36°K. This value corrected to 760 mm. gives 20.40°K. or −252.76°. This is an excellent agreement with the −252.78° of the Reichsanstalt and −252.75° of Leiden.[14]

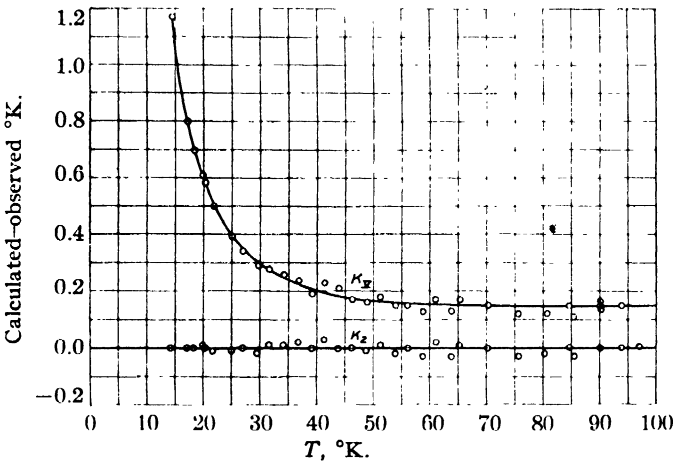

Fig. 1.—Deviation of platinum resistance thermometers K_2 and K_V from values given in reference table (II).

To show that the bulb had come to the temperature of the bath the resistances of the two platinum thermometers were compared with values previously obtained by direct immersion in a bath of boiling hydrogen. After making the proper correction for pressure differences, K_2 gave a resistance 0.0001 ohm higher and K_v 0.0001 ohm lower than previously, these variations being within the limits of error of the measurements.

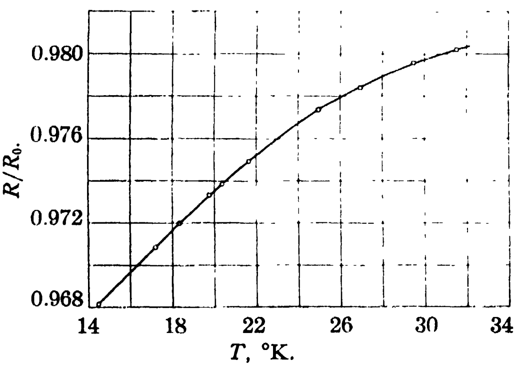

Fig. 2.—R/R_0 values for a constantan thermometer in the region of high sensitivity.

Henning[4] has published the deviation formula $R/R_0 - R'/R'_0 = (T - 273)[A - B/(T + 10)]$ for the range 20 to 80°K. without presenting data on which it was based. R/R_0 and R'/R'_0 refer to two thermometers at absolute temperature T; A and B are constants. The data of Table I furnish a test of this equation. Using K_2 and K_v for the two thermometers and evaluating A and B from the data for 21.66 and 90.19°K., no deviation equivalent to greater than 0.01° in $R/R_0 - R'/R'_0$ was found from 20 to 97°K.

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(14) Heuse and Otto, *Ann. Physik*, [5] **9**, 486 (1931); Keesom, Bijl and van der Horst, *Leiden Comm.*, No. 217 (a); *Proc. Amst. Akad.*, **34**, 78 (1931).

Henning and Otto[3] have recently given values of R/R_0 at eight temperatures between 14 and 80°K. for four Reichsanstalt thermometers and one from Leiden. If this formula and the table for K_2 are used to calculate values of R/R_0 for these thermometers, no difference between observed and calculated values equivalent to more than 0.07° is found for any of the three thermometers of the purest platinum even though the values of R/R_0 at 20°K. vary from 0.0065 to 0.0092. For their thermometer No. 35, for which the values of R/R_0 are most nearly equal to those for K_2, the difference does not exceed 0.03°. We believe that the reference table given for K_2 together with Henning's formula should give values correct within 0.05° in the range 20 to 90°K., providing the unknown thermometer is calibrated at the boiling points of hydrogen and oxygen and has characteristics similar to those of K_2. For exact work, however, a direct comparison such as here carried out must be recommended.

The simplified four constant equation recommended by Henning and Otto[3] was also tested on K_2. Errors of as much as 0.11° were found in the computed values. When the temperatures chosen for evaluation of the four constants were changed, the constants were changed in both sign and magnitude.

The authors are indebted to Dr. F. G. Brickwedde for his help and encouragement in this work. The assistance of Mr. R. A. Nelson in the measurements and calculation, and of Mr. J. W. Cook in liquefying the hydrogen, is gratefully acknowledged.

Summary

1. A constant volume gas thermometer for use in the calibration of resistance thermometers between 14 and 90°K. has been constructed.

2. The resistance of specimens of platinum, platinum–10% rhodium and constantan has been determined in this range with an estimated error of about ±0.02°.

3. A reference table of R/R_0 for platinum between 14 and 109°K. and for constantan between 14 and 26°K. has been constructed giving values for every degree in this interval.

4. The usefulness of Henning's two constant deviation formula in conjunction with this reference table has been demonstrated.

WASHINGTON, D. C.

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[Contribution from the Department of Chemistry, Cornell University]

Germanium. XLI. Some New Salts of Fluogermanic Acid[1]

By L. M. Dennis and B. J. Staneslow

with Microscopical Studies by W. D. Forgeng

The fluogermanates of the alkali metals and of silver, thallium and barium are already known. The present article describes compounds of this acid with several nitrogen bases.

Experimental

The preparation and purification of the several salts were carried out entirely in platinum apparatus. The purity of each salt was confirmed by spectroscopic examination.

Fluogermanic acid was prepared from pure germanium dioxide and Baker's "c. p." 40% hydrofluoric acid. The bases were Kahlbaum purest grade except ammonia, which was purified in the laboratory.

Ammonium Fluogermanate.—Purified ammonia was passed through a platinum tube into a cooled solution of fluogermanic acid; a white, gelatinous solid formed. This was collected on a filter, dissolved in a small amount of water, was then slightly acidulated with hydrofluoric acid and reprecipitated with ethyl alcohol. The precipitate was dissolved in a very dilute solution of hydrofluoric acid, and was fractionally crystallized from this solution. The end fractions were discarded. The middle fractions were combined and again fractionally crystallized.

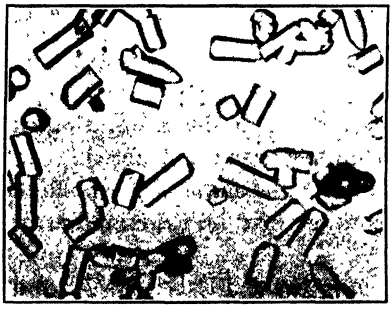

Fig. 1.—Ammonium fluogermanate (× 86).

Optical Properties.—The crystals of ammonium fluogermanate (Fig. 1) are apparently combinations of hexagonal prisms and bipyramids. Occasional hexagonal plates also occur.

The prismatic views show parallel extinction with very weak double refraction. The plate-like crystals are isotropic and give a good uniaxial interference figure. The material is optically negative. Refractive indices: (ϵ) = 1.425; (ω) = 1.428.

This salt is crystallographically similar to the hexagonal modifications of ammonium and potassium fluosilicate.

Hydroxylamine Fluogermanate.—In one synthesis, hydroxylamine, and in another, hydroxylamine hydrochloride, was added to a cooled solution of fluogermanic acid. The clear solution was fractionally crystallized as for the ammonium salt. A sample from the middle fractions, dried by pressing between filter paper, was found on analysis to be the dihydrate, $(NH_2OH)_2 \cdot H_2GeF_6 \cdot 2H_2O$.

Optical Properties.—The tabular crystals of hydroxylamine fluogermanate dihydrate are monoclinic prisms 110, and orthopinacoids 100 terminated by clinodomes 011 (Fig. 2).

Observed perpendicular to 100, the crystals show parallel or symmetrical extinction, with weak double refraction. The interference figure for the view indicates that the acute bisectrix is approximately perpendicular to this face.

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by B. J. Staneslow in partial fulfilment of the requirements for the degree of Master of Chemistry.

Crystals lying on 110 show slightly oblique extinction, with strong double refraction. Clinopinacoidal views of the crystals are rare. They show an angle β of about 80°, and an extinction angle of about 35°.

The material is biaxial, negative, with $2V$ about 60°, and fairly strong dispersion, $r > v$. $B_{x_a} \wedge a = 80°$. The axial plane is 010. Refractive indices: $(\alpha) = 1.418$; $(\beta) = 1.438$; $(\gamma) = 1.443$.

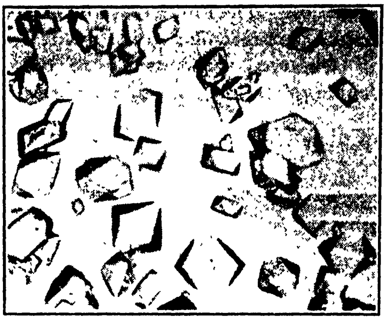

Fig. 2.—Hydroxylamine fluogermanate dihydrate (× 80).

Hydrazine Fluogermanate.—A 50% solution of hydrazine hydrate was added to a cooled solution of fluogermanic acid. On addition of 95% ethyl alcohol the salt separated out in colorless plates. The compound was purified by repeatedly dissolving it in water that was slightly acidified with hydrofluoric acid, and throwing out the salt from this solution by ethyl alcohol. The compound separates in the anhydrous form.

Optical Properties.—Hydrazine fluogermanate crystallizes as monoclinic prisms with basal and orthopinacoids (Fig. 3). Crystallized on a slide, they lie on either pinacoid face 001 or 100, or on a prism face 110. Clinopinacoid faces are occasionally developed, and when lying on these faces, the crystals show an angle β of about 80°.

Observed perpendicular to 001 or 100, the crystals exhibit parallel or symmetrical extinction, with very weak double refraction. Interference figures of these views indicate that 010 is the axial plane.

Crystals lying on 110 show oblique extinction, the angle being about 30°.

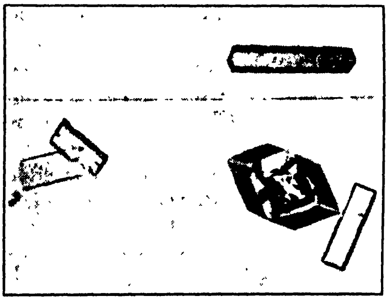

Fig. 3.—Hydrazine fluogermanate (× 86).

The material is biaxial, negative, with $2V$ near 90°. The axial plane is 010. Refractive indices: $(\alpha) = 1.452$; $(\beta) = 1.460$; $(\gamma) = 1.464$.

Aniline Fluogermanate.—A solution of fluogermanic acid was run into a solution of aniline in 95% ethyl alcohol, the latter being in slight excess. On cooling the solution in ice, fine, white crystals separated. These were collected on a filter, were washed with cold alcohol to remove the excess of aniline, and purified by recrystallization from hot alcohol. The solubility in alcohol was lowered by the addition of ether. The pure salt is white, but gradually turns light yellow on exposure to air.

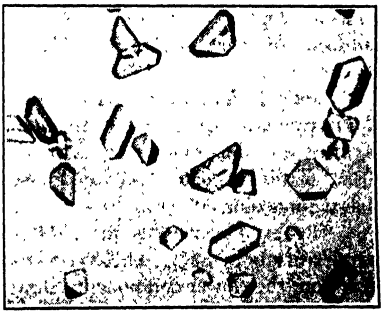

Fig. 4.—Aniline fluogermanate (× 80).

Optical Properties.—The tabular crystals of aniline fluogermanate are monoclinic prisms

110, with ortho 100 and basal pinacoids 001. Clinopinacoid and hemipyramid faces are also developed (Fig. 4).

When lying on 001, the crystals show parallel extinction with very weak double refraction. The interference figure for this view shows the optic normal to be approximately perpendicular to the *C* axis.

Observed perpendicular to 100, the crystals show parallel extinction with weak double refraction. Interference figures show an optic axis at an angle of about 30° to the perpendicular of this face.

Crystals lying on the clinopinacoidal faces 010 are flattened. They show an angle β of about 85° and an extinction angle of about 80°. No interference figure is obtained for this orientation.

The substance is biaxial, negative, with $2V$ about 35°, dispersion strong $r > v$. Axial plane is 010.

Refractive indices: $(\alpha) = 1.471$; $(\beta) = 1.532$; $(\gamma) = 1.541$.

Monomethylaniline Fluogermanate.—The method was similar to that used for the aniline salt. Recrystallized from hot 85% ethyl alcohol, washed with 95% alcohol and ether: crystals, white needles, anhydrous.

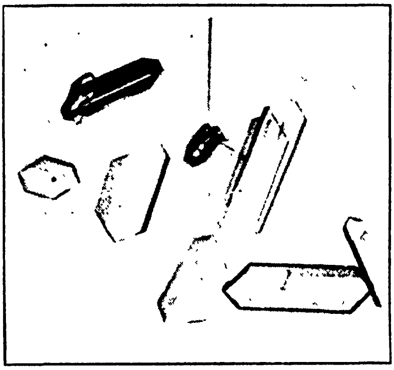

Fig. 5.—Monomethylaniline fluogermanate (× 100).

Optical Properties.—The crystals of monomethylaniline fluogermanate are apparently orthorhombic prisms 110 terminated by domes 011. The terminal angle between two dome faces is about 100° (Fig. 5).

Prismatic views show parallel extinction with fairly strong double refraction. The axial plane is parallel to 001. The acute bisectrix is perpendicular to 100. Good interference figures are obtainable.

The material is biaxial, negative, with $2V$ about 60°, $r > v$ strong; optical orientation: $X = a$; $Y = c$; $Z = b$; $B_{x_a} = a$

Refractive indices: $(\alpha) = 1.472$; $(\beta) = 1.562$; $(\gamma) = 1.565$.

Dimethylaniline Fluogermanate.—The method of preparation was similar to that used for aniline fluogermanate. Recrystallized from hot 95% ethyl alcohol with precipitation from the alcoholic solution by the addition of ether; white, crystalline, stable in the air.

Optical Properties.—Dimethylaniline fluogermanate crystallizes in the monoclinic system as clinodomes 011, clinopinacoids 010, orthopinacoids 100, and occasional basal pinacoids 001 (Fig. 6).

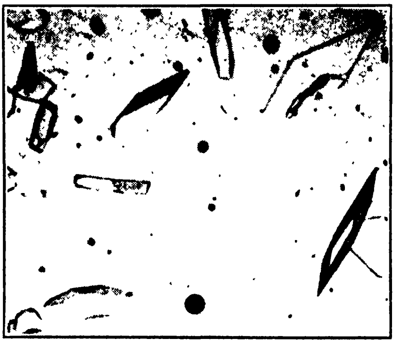

Fig. 6.—Dimethylaniline fluogermanate (× 80): (see summary)

Observed perpendicular to 100, the crystals are rhomb-shaped in outline with acute angles of about 35°. This view shows symmetrical extinction with strong double refraction, the slower component vibrating parallel with the acute diagonal. Interference figures for this view show the axial planes to be roughly parallel with 010.

Crystals developed so as to lie on 100 are flattened and show parallel extinction with weak double refraction. The interference figure indicates an optic axis at an angle of about 45° to the normal for this view.

Clinopinacoidal views show an angle β of about 30° and an extinction angle of about 40°. Both optic axes lie outside this view.

The material is biaxial, positive or negative, with $2V$ about 90°. Axial plane is 010. Refractive indices: $(\alpha) = 1.445$; $(\beta) = 1.53 \pm 0.005$; $(\gamma) = 1.617$.

The analyses, densities and solubilities of the six salts are given in the table.

No.		d_{25}^{25}	Solubilities Water	CH₃OH	C₂H₅OH	Other organic solvents
1	$(NH_4)_2GeF_6$	2.564	s.	i.	i.	i.
2	$(NH_2OH)_2 \cdot H_2GeF_6$	2.492[a]	s. hyd.	s. absol.	v. sl. s.	v. sl. s.
3	$(N_2H_4)_2 \cdot H_2GeF_6$	2.406	s. hyd.	v. sl. s.	v. sl. s.	v. sl. s.
4	$(C_6H_5 \cdot NH_2)_2 \cdot H_2GeF_6$	1.579	s. hyd.	s.	s. hot	i.
5	$(C_6H_5 \cdot NHCH_3)_2 \cdot H_2GeF_6$	1.631	s. hyd.	s.	sl. s. hot	i.
6	$(C_6H_5 \cdot N(CH_3)_2)_2 \cdot H_2GeF_6$	1.548	s. hyd.	s.	s.	i.

[a] Density of $(NH_2OH)_2 \cdot H_2GeF_6 \cdot 2H_2O$ is d_{26}^{26} 2.229.

		Analyses					
				% F		% Ge	
No.		Found	Calcd.	Found	Calcd.	Found	Calcd.
1	NH_3	16.22	16.20	51.41	51.20	32.59	32.61
2	NH_2OH	25.93	25.94	44.93	44.76	28.55	28.51
3	N_2H_4	25.35	25.36	44.84	45.11	28.8	28.73
4	N	7.31	7.48	30.33	30.42	19.47	19.37
5	N	7.00	6.96	28.2	28.30	18.01	18.03
6	N	6.38	6 50	26.42	26.46	17.01	16.85

In the analyses, ammonia was determined by distillation with sodium hydroxide and titration of the distillate; fluorine by the method of Starck;[2] hydroxylamine by titration with potassium permanganate;[3] hydrazine by the method of Kolthoff;[4] nitrogen in $(C_6H_5 \cdot NH_2)_2 \cdot H_2GeF_6$, $(C_6H_5 \cdot NHCH_3)_2 \cdot H_2GeF_2$ and $(C_6H_5 \cdot N(CH_3)_2)_2 \cdot H_2GeF_6$, by the modified Kjeldahl–Gunning–Arnold method with absorption of the ammonia in 4% solution of boric acid.[5] Copper sulfate was used instead of mercuric oxide.

Germanium was determined by direct precipitation of GeS_2[6] except that in the analyses of the hydrazine, aniline, monomethylaniline and dimethylaniline salts, it was found necessary first to expel the base by boiling the solution of the salt with an excess of potassium carbonate, or fusing the salt with an excess of potassium hydroxide.

Densities were determined by the pycnometric method, with toluene as the immersion liquid.

The melting points could not be determined with the apparatus of Dennis and Shelton[7] because of dissociation.

[2] Starck, *Z. anorg. Chem.*, **70**, 173 (1911).

[3] Bray, Simpson and MacKensie, THIS JOURNAL, **41**, 1363 (1919).

[4] Kolthoff, *ibid.*, **46**, 2009 (1924).

[5] Markley and Hann, *J. Assoc. Off. Agr. Chem.*, **8**, 455 (1925).

[6] Johnson and Dennis, THIS JOURNAL, **47**, 790 (1925).

[7] Dennis and Shelton, *ibid.*, **52**, 3128 (1930).

Summary

This article presents details concerning the preparation, analysis, properties and optical characteristics of certain salts of fluogermanic acid with nitrogen bases. All of these salts are soluble in water, but are hydrolyzed with separation of hydrated germanium dioxide. Hydrolysis is especially pronounced in the case of dimethylaniline fluogermanate as is evidenced by the round spots in the photomicrograph of the salt.

The analogy between fluogermanates and fluosilicates is shown by the formation of a dihydrate in the case of the hydroxylamine salts whereas the ammonium and hydrazine salts are anhydrous.

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x-Ray Studies of Fatty Acids[1,2]

BY F. B. SLAGLE AND EMIL OTT

Introduction

The long spacings of normal fatty acids have been measured by a series of investigators.[3] However, most of this work is not reliable, due in part to insufficient purity of the acids used. Due to the fact that we had a series of acids of exceptional purity available, it seemed worth while to repeat such measurements with increased accuracy. This was especially desirable in view of the study of mixtures of such acids which will be reported in a following paper.

Experimental Procedure

A. **Spectrograph.**—In all the work reported here a Bragg spectrograph (made in the Seeman Laboratory, Freiburg, i. Br.) with the approximate radius of 16.79 cm. was used. The adjustable front slit was set at 0.1 mm. during all of this work. Most of the measurements of the fatty acids were made by rotating the crystal at constant speed through the angle from 0 to ±10°, since we were only interested in the lower order reflections. The reflections were registered on Eastman x-ray films.

B. **x-Ray Source.**—x-Rays were obtained from a Seeman metal tube, using a tungsten filament and a copper target, the operating peak voltage being 40 kilovolts at 20 milliamperes. A nickel filter of 0.02 mm. thickness was used over the window of the tube at all times to cut out the β-radiation from the copper. The target of the tube was periodically cleaned, thus avoiding tungsten radiation, which under the worst conditions was found by spectrographic measurements to be less intense than the β-radiation from the copper after passing through the nickel filter. The β-radiation was never observed for the fatty acid reflections.

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[1] From a thesis submitted by F. B. Slagle, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Emil Ott and F. B. Slagle, compare preliminary note, *J. Phys. Chem.*, **37**, 257 (1933).

[3] Compare P. P. Ewald and C. Hermann, "Strukturbericht (1913–1928)," Akademische Verlagsgesellschaft, Leipzig, 1931, pp. 691–700.

C. Calibration of the Spectrograph.—Since the spectrograph was built with moderate precision only, it was found necessary to calibrate the instrument with utmost care in the angular range of the contemplated measurements. The reflections from mica do not completely cover this range when copper radiation is used, but the use of silver radiation eliminates this difficulty. It was found advisable to standardize the mica used against calcite, instead of using the mica values given by Siegbahn.[4] Actually we found appreciable deviation, which is to be expected in view of the chemical variations in mica. The fact that various micas have different *c*-spacings is also borne out by the work of Rinne[5] and Mauguin.[6]

The calibration of the spectrograph was then accomplished as follows. The first order reflection from the rhombohedral face of pure calcite (obtained from Dr. W. M. Thornton, Jr., of this Laboratory) is registered on a photographic film. The distance L between the corresponding reflections on either side of the primary beam is measured with a microcomparator to 0.01 mm. A correction for film shrinkage is obtained by imprinting on the undeveloped film in various places two points of known distance apart. This mode of measurement is applied in all cases. The third-order reflection of mica falls very close to the observed calcite reflection (Cu-radiation is used), and thus permits an accurate determination of the observed glancing angle Θ. From this third-order reflection, the other orders of mica are calculated according to Bragg's law. It is now possible to plot Θ against L. To obtain further calibration points the various reflections of mica are also obtained with silver radiation. We are thus enabled to obtain the Θ values of unknown substances by measurement of their L values.

The exact calculations of Θ used in this calibration should be given. The ordinary Bragg equation, $n\lambda = 2d \sin \Theta$ does not apply exactly when the index of refraction differs from unity. The corrected equation takes the form[4]

$$n\lambda = 2d\left(1 - \frac{4d^2}{n^2}\frac{\delta}{\lambda^2}\right)\sin \Theta$$

Siegbahn[4] gives the values of d from the rhombohedral face for calcite as calculated from the various orders, and it is observed that d becomes larger for the higher orders and approaches a constant value. The observed value for the first-order reflection of calcite is given as $d_1 = 3.02904$ Å.[4] From the ordinary Bragg's law ($n\lambda = 2d \sin \Theta$) we obtain the value of Θ for this first-order reflection. From the measurement of L, the effective radius, r, in the vicinity of the reflection is calculated. This value of r will be applicable to the third-order reflection of mica. Thus d_3 for mica is determined as 9.93447 Å. Knowing $\delta/\lambda^2 = 3.86 \times 10^{-6}$,[4] the true spacing d may be determined as follows

$$\text{since } d_n = d\left(1 - \frac{4d^2}{n^2}\frac{\delta}{\lambda^2}\right), \text{ it follows}$$
$$9.93447 = d(1 - (4d^2/9) \times 3.86 \times 10^{-6}) \text{ or}$$
$$d = 9.93615 \text{ Å}.$$

The value for any d_n may now be calculated, and by use of the ordinary Bragg's law again, the values of Θ may be calculated for any order and used in the calibration. Thus we obtain a plot of true angles against L.

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(4) Manne Siegbahn, "Spektroskopie der Röntgenstrahlen," Verlag Julius Springer, Berlin, 1931.

(5) F. Rinne, *Z. Krist.*, **59**, 230 (1924).

(6) Ch. Mauguin, *Compt. rend.*, **186**, 879 1131 (1928).

This calibration curve is used in the determination of the Θ values of the fatty acids. For the calculation of the d values, the corrected Bragg formula should be used (δ/λ^2 is not known). However, it is found that within the limits of the accuracy of the determinations, no systematic deviations are found when the ordinary Bragg's law is applied.

In cases with sharp lines the agreement for different orders is within one-tenth of one per cent. This accuracy is reproducible with different mountings of the sample, as well as with different chemical preparations. With broadened lines the accuracy is within five-tenths of one per cent. This precision appears to be higher than any previously obtained.

The values of the wave lengths used throughout this work are those given by Siegbahn.[4]

D. Measurement of Films.—On all of the pictures obtained from the fatty acids there were some strong lines (odd orders), and some weak lines (even orders). The accuracy of measurement of these lines depends on their strength and their sharpness. The strong, well-defined lines were measured with a microcomparator and the measurements could be checked to 0.01 mm. The weak lines were measured with a millimeter scale. The lines of intermediate strength were measured with either the microcomparator or the scale, depending upon the individual case.

In order to obtain the best value for each line, a series of measurements was taken on that line and the average value so obtained reported. All of the measurements of lines given in the tables to follow will be such average values. Those measurements which were made with the microcomparator will be marked (com.). All other lines were measured with the millimeter scale.

E. Preparation of Samples.—A short description of the three methods of preparing the samples is as follows:

(a) **Crystallization from Acetone.**—A few drops of an acetone solution of the pure acid were put on a glass plate and the acetone allowed to evaporate off. By regulating the rate of evaporation and the concentration of the acetone solution, it is very easy to obtain a uniform deposit on the plate of about 0.1 mm. in thickness.

(b) **Melting on Glass Plate.**—The technique for preparing samples by this method was more difficult. If a small amount of the acid is melted on a glass plate, it will persistently form a drop and not spread over the surface of the glass. If enough of the material is used a layer of the acid can be formed on the glass plate upon cooling, but such a layer will be very thick (about 1.0 mm.) and show very poor orientation. It was found necessary to form a much thinner film on the plate, causing longer exposure time. By spreading a small drop of the acid over the surface of the glass plate, and cooling rather rapidly (to avoid coalescence to a single drop) such thin films, of practically uniform thickness, can be deposited.

(c) **Pressing of Solid Sample on Glass Plate.**—If sufficient pressure is exerted upon a solid fatty acid it can be made to adhere to a glass plate. By pressing the acid between two glass plates it was found that the sample would spread to a uniform thickness. If the sample thus formed is thin, one of the glass plates can be removed so that all of the acid will remain in a thin film on the other glass plate. Samples prepared by this method are somewhat thicker than those prepared by the other methods and the reflection lines obtained are broadened.

F. Source of Acids.—The acids, C_{10} to C_{18}, used in this research were prepared by Dr. J. D. Meyer[7] and Dr. John Ruhoff under the direction of Prof. E. E. Reid. The

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(7) J. D. Meyer and E. E. Reid, THIS JOURNAL, 55, 1574 (1933).

methods of preparation and purification are given in detail in dissertations submitted by them to the Johns Hopkins University in 1932. In addition the C_{19} acid was prepared by the author according to the same methods.

It is believed that the purity of these acids is 99.5% or better (judging from the cooling curves which were obtained), which appears to be purer than the acids used by the other investigators in this field.

G. x-Ray Measurements on the Pure Acids.—The pure acids ranging from C_{10} to C_{19} have been studied with samples prepared by the three methods given previously. All these pictures were taken at room temperature (23 to 28°) excepting for C_{10} and C_{11} which, due to their low melting points, were taken at a slightly lower temperature (20 to 22°) in order to be sure that the sample remained solid during the exposure. The effect of this temperature variation upon the spacing of the (001) planes is easily within experimental error. In the case of the hydrocarbons, Müller[8] found that the expansion along the *c*-axis between liquid air temperatures and room temperatures was so small as to be unmeasurable. Dr. D. A. Wilson of this Laboratory has, in the case of C_{15} acid, observed a slight variation in the spacing between −50 and +25°. This sample, which was prepared by crystallization from acetone, gave a spacing of 35.63 ± 0.05 Å. at 25°,

TABLE I

The letter A, B, C or D before each value stands for the modification as listed by Francis, Piper and Malkin. The values marked (*) will be explained in the discussion. The setting points given above are taken from the dissertation of Dr. J. D. Meyer, excepting for C_{19} which was determined by the author. Cooling curves for these acids are also given by Dr. Meyer.

Acid	Setting points	Melted	Acetone	Pressed	Piper's values
C_{10}	31.19	(C)23.02	(C)23.02	(C)22.95	......
C_{11}	27.77	(C)25.32	(C)25.40	(C)25.22	......
C_{12}	43.22	(C)27.18	(C)27.18	(C)27.31	(C)27.4
C_{13}	41.55	(A)34.92 (B)31.27	(A)34.92	(A)34.84	(A)35.3 (B)31.65
C_{14}	53.86	(C)31.44	(C)31.39	(C)31.26 36.64	......
C_{15}	52.26	(B)35.75 (A)39.88	(B)35.63	(B)35.67	(B)35.8 (A)40.0
C_{16}	61.82	(C)35.52	(C)35.47 (B)39.35	(C)35.53	(C)35.65 (B)39.1
C_{17}	60.66	(C)38.57	(B)39.98	(B)40.05 (D)32.85 (A)44.42	(B)40.5 (D)33.9 (C)38.6
C_{18}	68.82	(C)39.83	(C)39.62 (B)44.14 (A)46.15	(C)39.92 (B)44.14 (A)46.29	(C)39.95 (B)44.0 (A)46.6
C_{19}	67.64	......	(B)44.13	(B)44.37* (B)44.14*	(B)44.5

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(8) A. Müller, *Proc. Roy. Soc.* (London), **A127**, 417 (1930).

and a spacing of 35.19 ± 0.10 Å. at −50°. This change in spacing of 0.44 Å. corresponds to a temperature change of 75°, or a change of 0.00587 Å. per degree.

Table I gives the best value for the spacings obtained by the three methods of preparation together with the corresponding values reported by Francis, Piper and Malkin[9] and the setting points of the acids. Fig. 1 gives the plot of the spacings obtained for the pure fatty acids.

The following typical results will demonstrate the check obtained for the spacing from the successive orders (starting with the first order).

	C_{16} Acid melted on glass plate sin Θ/*n*	C_{13} Acid crystallized from acetone on glass plate sin Θ/*n*	C_{12} Acid pressed on glass plate sin Θ/*n*
	0.02167 (com)	0.02204 (com)	0.02815 (com)
	.02167 (com)	.02204	.02814
	.02166 (com)	.02203 (com)	.02819 (com)
	.02162 (wk)	.02202	.02817
	.02165 (com)		
	.02164		
Average	.02166	.02203	.02816
d	35.52 Å.	34.92 Å.	27.32 Å.

(com) = comparator measurement. (wk) = weak line.

A check was made on several acids to see how reproducible the results were. The samples were crystallized again on a glass plate, using the same method of crystallization and the sample remounted in the spectrograph. The values obtained with maximum deviations were

C_{10} (melted sample)	23.03 ± 0.03; 23.04 ± 0.04; 23.00 ± 0.06
C_{11} (melted sample)	25.31 ± 0.03; 25.30 ± 0.03; 25.27 ± 0.04; 25.32 ± 0.03; 25.34 ± 0.03
C_{12} (melted sample)	27.20 ± 0.01; 27.16 ± 0.02; 27.18 ± 0.02
C_{12} (pressed sample)	27.29 ± 0.02; 27.32 ± 0.03
C_{13} (melted)	34.91 ± 0.03; 34.92 ± 0.04
C_{16} (crystallized from acetone)	35.44 ± 0.07; 35.50 ± 0.06
C_{17} (crystallized from acetone)	39.98 ± 0.06; 39.98 ± 0.07
C_{18} (melted)	39.86 ± 0.04; 39.80 ± 0.06
C_{18} (crystallized from acetone)	39.62 ± 0.07; 39.62 ± 0.07
C_{19} (crystallized from acetone)	44.07 ± 0.07; 44.19 ± 0.10

Since the samples were prepared, using essentially the same methods, by two independent workers, samples of C_{12} and C_{13} were used to check the reproducibility of the chemical preparation.

	Sample I	Sample II
C_{12}	27.20 ± 0.01	27.18 ± 0.03; 27.16 ± 0.02
C_{13}	34.91 ± 0.02	34.02 ± 0.01

C_{11} was prepared by two entirely different methods: (1) by hydrogena-

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(9) F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A128**, 214 (1930).

tion of undecylenic acid and (2) by the alcohol–bromide–cyanide method from C_{10}. The results were

Hydrogenated Undecylenic	25.32 ± 0.03; 25.34 ± 0.03; 25.31 ± 0.03; 25.30 ± 0.03
Alcohol–Bromide–Cyanide	25.27 ± 0.04

The measurements for an entirely new modification of C_{14} acid are given. For the first five orders (fourth order is too weak for measurement), it is observed $\sin \Theta/n$ = 0.02103 (wk); 0.02103 (com), 0.02102 (wk) and 0.02094 (wk); average 0.02100; d = 36.64 Å.

This new modification of C_{14} was checked by preparing a new pressed sample which gave the value 36.64 Å., the maximum deviation being in both cases 0.05 Å.

Discussion of Results

From the data given it is seen that the results obtained for any one acid by a single method of preparation of the sample, except for the case of the pressed sample of C_{19}, give spacings which check within the experimental error. These results were not only reproducible with the same sample of the acid, but also with different samples of the acid prepared by the same methods by two independent investigators. It was also found in the case of undecylic acid (C_{11}) that the results were reproducible for two entirely different methods of preparation of the acid. This wide range of reproducibility, combined with the increased accuracy, permits the use of the reported substances as useful standards, where long spacings are desired.

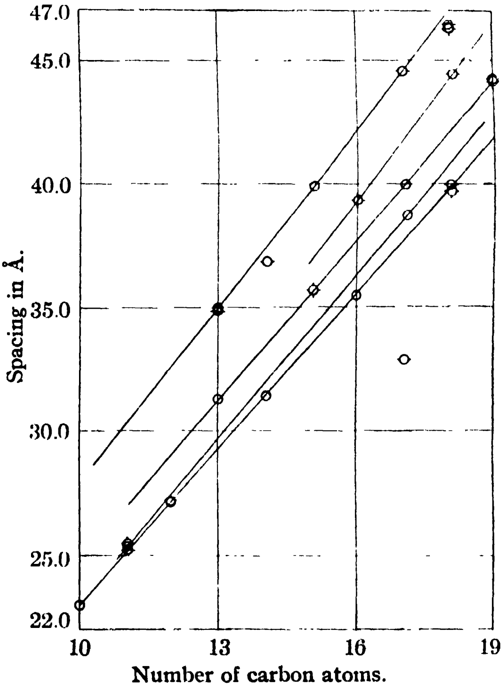

Fig. 1.—Pure acids: O, melted sample; -O-, pressed sample; -ǫ-, sample crystallized from acetone.

In Table I are given our values for the spacings of the pure acids as compared with those obtained by Francis, Piper, and Malkin.[9] In many cases there is a real difference which is sometimes as much as one per cent. In most cases our values are lower than those of Piper.

From the data given it is observed that there are deviations, which appear to be outside of the experimental error, between the spacings obtained for the same modification of a single acid, depending upon the method of preparation of the samples. Piper, Malkin and Austin[10] found similar variations for various long-chain compounds which in some cases were as much as one per cent. Their variations, in the case of fatty acids, were not more than one-half of one per cent., which is comparable with our findings.

If the values obtained from the melted samples and from those crystallized from acetone are compared, it is seen that the lower members of the fatty acid series check very well (except for C_{11}). The higher members (C_{14} and above) deviate giving a value for the melted sample which is higher than the acetone value. A possible explanation for these facts is as follows. The acetone samples were all obtained by evaporating the solutions at room temperature. For these samples the crystallization took place rather slowly, and there were no strains set up due to temperature changes on the solid after it was once formed. The samples crystallized from the melt were formed at their respective setting points, and then cooled to room temperature. In the case of the higher members of the series this crystallization took place very rapidly. The subsequent cooling of these samples gave additional strain, leading to a slightly different tilt of the chains.

The deviations between the pressed sample values and the melted or crystallized from acetone values do not show any regularity. Since these samples were prepared by exerting pressure on the solid acid, it was thought, in analogy to the explanation mentioned above, that the pressure might change the spacing slightly, and thus account for the observed variation. This point is very hard to test because of the difficulty in obtaining equal pressures on all portions of the acid. An attempt was made to test this theory, in the case of C_{19} acid. A pressed sample upon which very little pressure had been exerted gave a spacing of 44.37 Å. A pressed sample upon which much pressure had been exerted gave a spacing of 44.14 Å. This difference seems to be greater than the experimental error in the two measurements. The shift in the spacing is in the right direction, and would seem to substantiate the proposed explanation. This small variation with varying pressure might also be the cause for the decrease in sharpness of the reflections in the case of the pressed samples.

From an inspection of Fig. 1 it is seen that a plot of the spacing obtained against the carbon content of the acids gives a series of straight lines, as has already been known. According to the previous discussion, the spacings obtained from the samples which were crystallized from acetone are the most accurate values. If these spacings are considered, it is seen that the linear dependence with the carbon content is fulfilled, even with the increased accuracy obtained in this work. Also, as has already been

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(10) S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926).

known, the even and odd acids fall on separate lines. This indicates a different tilt in corresponding even and odd modifications. Malkin[11] has offered a simple explanation for this phenomenon. According to his picture there would also exist in the case of tilted chains a difference in packing of the end links of the chains of even and odd acids. This difference is supposed to account for the alternation in melting points. We find that the C_{11} acid, although belonging to a different line, lies nearly on the line connecting the C_{10} and C_{12} acids. This would indicate practically identical tilt of the chains, provided the end groups were arranged correspondingly. A very decided alternation in the melting points, however, forces us to assume a difference in the arrangement of the end groups.

We have further independent evidence of such a difference in arrangement. We observe that in all the modifications (A, B and C, as far as we could obtain them) of the acids, the even orders of the even acids are relatively stronger than the even ones in the odd series (of course in all these cases the even orders are always of lower intensity than the odd ones, in the range of orders studied by us). Since the relative strength of the orders is a function of the density along the chains, this means that the packing of end groups is different in odd and even cases.

Such difference in packing is further shown in the discovery of a new modification in the case of the C_{14} acid (pressed sample). The spacing of this modification does not seem to fit any previously known modification with sufficient accuracy. The most remarkable difference is, however, to be found in the intensity distribution. It is found: first order, weak; second order, strong; third order, weak; fourth order, indicated; fifth order, weak.

As a rule we observe fewer modifications than Francis, Piper and Malkin[9] with similar treatment. This was true especially of the D modification, which was never found except for C_{17} (pressed), where it was just indicated. It will be seen, in the following paper, that a larger number of modifications is readily obtained in the case of mixtures. In view of the high purity of our acid samples and measurable differences in spacings from other authors, this might suggest differences in composition as an explanation for the above phenomenon.

Summary

The interplanar distances of the (001) planes have been measured for the series of very pure normal fatty acids ranging from C_{10} to C_{19}.

The values thus obtained are of higher accuracy than of any similar previous measurements.

Depending upon the method of preparation of the sample slight variations in the spacings are observed.

The C_{19} acid was prepared as a part of this investigation.

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[11] T. Malkin, *Nature*, **127**, 126 (1931); T. Malkin, *J. Chem. Soc.*, 2796 (1931).

An entirely new modification of fatty acids was discovered in the case of the C_{14} acid.

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x-Ray Studies of Mixtures of Fatty Acids[1,2]

BY F. B. SLAGLE AND EMIL OTT

Introduction

x-Ray studies on well-defined mixtures of long chain compounds are relatively few. Most of the results available so far we owe to Piper and his co-workers.[3]

Since we had a series of unusually pure fatty acids available and since we are particularly interested in mixtures of long chain compounds from the standpoint of polymerization, this study was undertaken.

Experimental

I. Two-Component Mixtures of Fatty Acids

1. General. (a) Preparation of Samples.—All samples of the mixtures were prepared by the same method. In each case, samples of the acids were weighed out to 0.0001 g. The acids were then fused together in a watch glass and kept just above the melting point for some time. Continual stirring with a small glass rod assured thorough mixing of the several components. The entire mass was then solidified by rapid cooling.

The sample plates were prepared by melting and subsequent solidification of portions of these mixed samples on glass plates. Whenever a check was run on any sample, a second portion of the mixture was taken solidified on a glass plate, and then remounted in the spectrograph. The materials used and the x-ray technique are the same as used in the previous investigation.[4]

(b) Explanation of Tables.—Whenever the deviation for a value is listed, it will be the maximum deviation from the mean in Ångström units. Where more than one value is listed for a particular mixture, it is a check on the reproducibility of the result, unless otherwise explained. The final

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[1] From a thesis submitted by F. B. Slagle in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Emil Ott and F. B. Slagle, compare preliminary note, *J. Phys. Chem.*, **37**, 257 (1933).

[3] Hydrocarbons: S. H. Piper, D. Brown and S. Dyment, *J. Chem. Soc.*, **127**, 2194 (1925); G. L. Clark, *Nature*, **120**, 12 (1927); S. H. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931). Acids: S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926); also F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A126**, 214 (1930).

[4] F. B. Slagle and Emil Ott, THIS JOURNAL, **55**, 4396 (1933).

column in the graphs represents the best value or values for the spacings of the (001) plane of the mixtures. The composition of all of the mixtures is given in mole percentages.

2. Systems with Components which Are One Carbon Atom Apart.—Mixtures of capric (C_{10}) and undecylic (C_{11}) acids were studied in ten equal steps. In Table I are listed the spacings obtained from these mixtures, and in graph I their plot is given. Figure 1 shows prints of three of the C_{10}–C_{11} mixtures together with pure C_{10} and pure C_{11}. It is observed that the lines obtained from the mixtures are comparable in sharpness with those obtained from the pure acids, and that each mixture gives a single spacing.

Table I

C_{10}–C_{11} Mixtures

Mole % C_{10}	Mole % C_{11}	Spacing with dev.		Av. spacing
0.0	100.0	25.32		25.32
10.7	89.3	25.03 ± 0.04		25.03
20.8	79.2	24.69 ± 0.03		24.69
30.2	69.8	24.55 ± 0.02		24.55
41.8	58.2	24.37 ± 0.04	24.39 ± 0.05	24.38
51.8	48.2	24.20 ± 0.01	24.20 ± 0.01	24.20
61.9	38.1	23.71 ± 0.01		23.71
71.4	28.6	23.58 ± 0.01		23.58
81.2	18.8	23.33 ± 0.00		23.33
90.7	9.3	23.19 ± 0.02		23.19
100.0	0.0	23.02		23.02

Typical results on these C_{10}–C_{11} mixtures are as follows: mole % C_{10} = 51.8; mole % C_{11} = 48.2; $\sin \Theta/n = 0.03179$ (com.), 0.03179, 0.03178 (com.) and 0.03182 (wk); average = 0.03179; d = 24.20 Å.

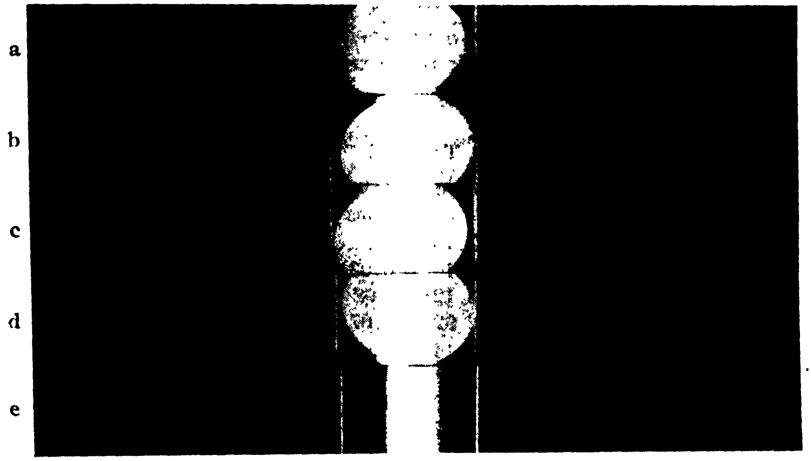

Fig. 1.—C_{10}–C_{11} acid mixtures: a, pure C_{10} acid; b, C_{10} = 81.2%; C_{11} = 18.8%; c, C_{10} = 61.9%; C_{11} = 38.1%; d, C_{10} = 30.2%; C_{11} = 69.8%; e, pure C_{11} acid.

3. Systems with Components which Are Two Carbon Atoms Apart. (a) C_{10}–H_{12} Acid Mixtures.—Table II gives the spacings obtained for the various mixtures of C_{10} and C_{12} fatty acids which were studied. It is observed that in the case of two of the mixtures more than one spacing is reported. That these spacings correspond to different modifications for these particular mixtures, and not to phases of different composition, was proved for the mixture of 43.8% of C_{10} and 56.2% of C_{12} as follows. The sample was prepared in the usual manner and a picture taken immediately. Two spacings were observable which were 25.12 Å. and 25.90 Å. The same sample plate was exposed two days later and gave two spacings: 25.08 Å. and 26.92 Å. After a total of two weeks, this sample plate was again exposed and this time just one spacing of 26.92 Å. was observed. Thus the spacing of 25.90 Å. observed on the first picture corresponds to a rather unstable modification which changes over completely to a second modification having a spacing of 26.92 Å. During this change the amount of the remaining modification corresponding to 25.10 Å. (average of 25.12 and 25.08) was practically unchanged, judging from the intensities of the lines. However, upon standing for two weeks it also changed to the modification with the spacing of 26.92 Å.

This same explanation holds for the mixture of C_{10} = 53.4% and C_{12} = 46.6%. Here, however, only two spacings are observed; the modification having the spacing of 26.14 Å. is present in small amounts, and upon standing changes over into a more stable modification which has the spacing of 25.31 Å.

Plots of the spacings obtained for the C_{10}–C_{12} mixtures are given in graph II. Prints of pure C_{10} and of pure C_{12} together with several of the mixtures are given in Fig. 2. Also in Fig. 2 are given prints of the mixture having the composition of 43.8% of C_{10} and 56.2% of C_{12} showing the changes in modification that took place when the sample was allowed to stand over a period of two weeks.

TABLE II

C_{10}–C_{12} MIXTURES

Mole % C_{10}	Mole % C_{12}	Spacing with dev.	Av. spacing
0.0	100.0	27.18	27.18
22.5	77.5	27.10 ± 0.03	27.10
43.8	56.2	25.12; 25.08 ± 0.03; 25.90	25.10
		26.92 ± 0.07; 26.92 ± 0.04	25.90 26.92
53.4	46.6	26.14 ± 0.02; 25.31 ± 0.02	26.14 25.31
63.2	36.8	24.94 ± 0.03	24.94
82.6	17.4	23.53 ± 0.05; 23.54 ± 0.04	23.54
100.0	0.0	23.02	23.02

A typical calculation on these C_{10}–C_{12} mixtures is as follows: mole % C_{10} = 22.5; mole % C_{12} = 77.5; $\sin \Theta/n$ = 0.02839 (com.), 0.02839, 0.02836 (com.) and 0.02842; average = 0.02839; d = 27.10 Å.

(b) C_{16}–H_{18} Acid Mixtures.—This work on mixtures of palmitic (C_{16}) and stearic (C_{18}) acids is a repetition of the work reported by Piper, Malkin and Austin[5] on these same two acids, except that the mixtures have slightly different compositions. Each mixture gave a single spacing, the lines for these mixtures being as sharp as those for the pure acids. Table III gives the spacings for the mixtures of C_{16} and C_{18} acids, and graph III gives the plot of these spacings.

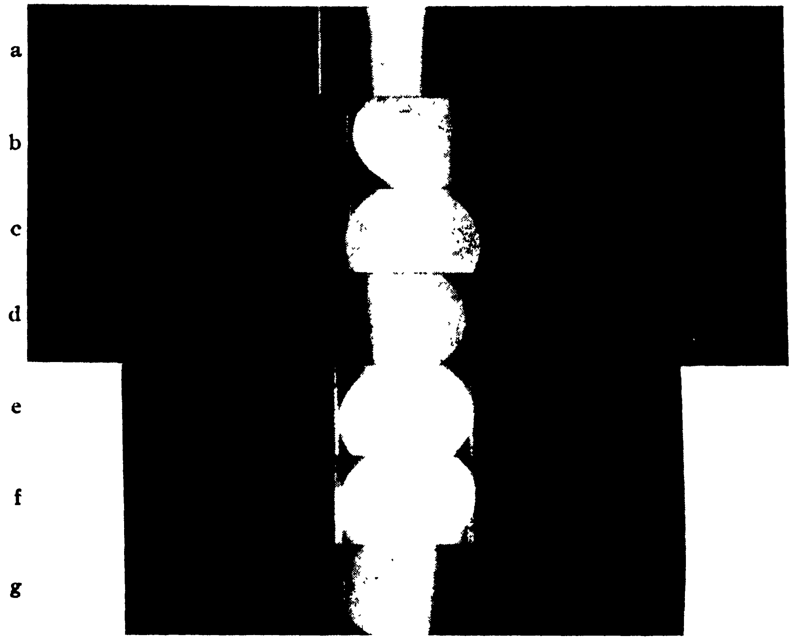

Fig. 2.—C_{10}–C_{12} acid mixtures: a, pure C_{10} acid; b, C_{10} = 63.2%; C_{12} = 36.8%; c, C_{10} = 53.4%; C_{12} = 46.6%; d, pure C_{12} acid. Effect of time on mixture: C_{10} = 43.8%; C_{12} = 56.2%: e, picture taken immediately; f, picture taken after 2 days; g, picture taken after 2 weeks. Sections b and c were placed incorrectly in making the illustration; they should have been reversed in position to match a and d.

TABLE III

C_{16}–C_{18} MIXTURES

Mole % C_{18}	Mole % C_{16}	Spacing with dev.	Av. spacing
100.0	0.0	39.83	39.83
89.3	10.7	39.72 ± 0.02	39.72
72.8	27.2	39.49 ± 0.04	39.49
47.5	52.5	38.50 ± 0.04	38.50
23.3	76.7	38.14 ± 0.02	38.14
9.3	90.7	35.88 ± 0.04	35.88
0.0	100.0	35.52	35.52

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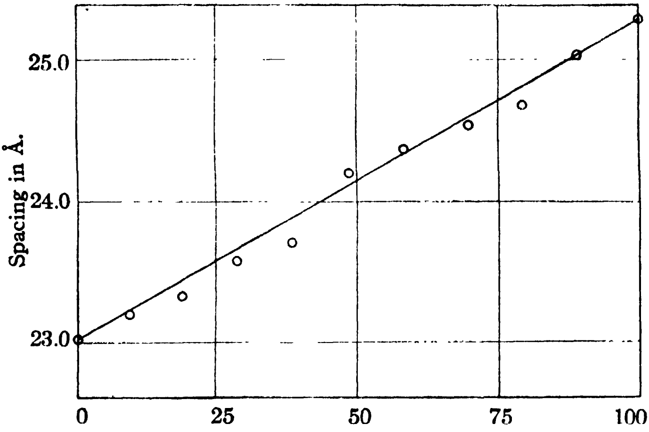
(5) S. H. Piper, T. Malkin and H. E. Austin, *J. Chem. Soc.*, **129**, 2310 (1926).

4. Systems with Components which Are Three Carbon Atoms Apart.—Francis, Piper and Malkin[6] report that combination spacings are obtained for equimolar mixtures of fatty acid chains of n and $n + 1$, n and $n + 2$, and n and $n + 3$ carbon atoms apart, but that equimolar mixtures of chains of n and $n + 4$ carbon atoms apart crystallize separately. They give, however, no data for such mixtures beyond the n and $n + 1$ equimolar mixtures, and fail to say anything about mixtures which are not equimolar.

In our work on mixtures of fatty acids of chain lengths n and $n + 3$ we have studied non-equimolar mixtures as well as equimolar ones. The principal studies were made on mixtures of C_{10} and C_{13} acids. The following results were obtained.



Graph I.—Mixtures of C_{10}–C_{11} acids.

(a) **Equimolar Mixture, Mole % C_{10} = 49.9; Mole % C_{13} = 50.1.**—Two separate sample plates were prepared and exposed. The spacings obtained were 26.30 Å.; 24.21 Å. and 26.29 Å.; 24.18 Å., respectively. The spacing corresponding to 24.20 Å. (average of 24.18 and 24.21) was calculated from a single first order which was very weak. As might be expected the spacing of 26.29 Å. falls on the odd acid curve corresponding to a carbon content of $11^1/_2$ carbon atoms.

(b) **Non-equimolar Mixture, Mole % C_{10} = 24.8; Mole % C_{13} = 75.2.**—Two separate samples of this mixture were prepared and exposed. Film (1) corresponds to the picture obtained from the sample which was crystallized slowly from the melt (approx. one-half minute). Film (2) corresponds to the picture obtained from the sample which was prepared by rapid crystallization from the melt (approx. two seconds). The spacings from the first case are 34.94; 28.87 and 26.36 and from the second case 34.95 and 29.59 Å.

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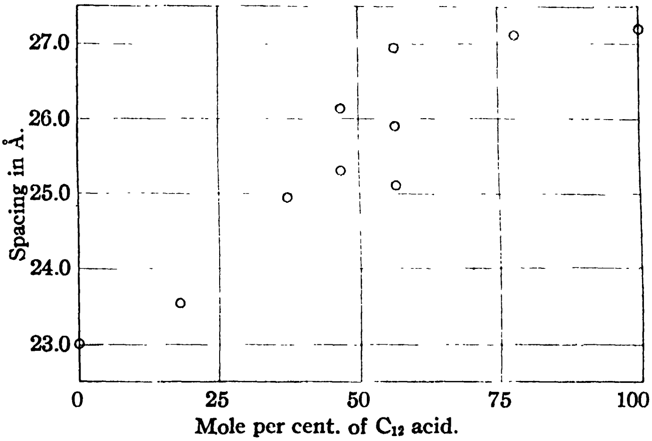
(6) F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.* (London), **A128**, 214 (1930).

From the results obtained here we can see that the speed of crystallization affects the results very markedly. It is seen that the sample which was prepared by slow crystallization from the melt gave three sets of lines, all of which were of equal intensity. The sample which was prepared by rapid crystallization gave only two sets of lines, one set being weak. The set of strong lines on this second film (spacing equal to 34.95 Å.) corresponds exactly to one of the sets of lines found on the first film. The weak set of lines on this second film (spacing equal to 29.59 Å.) does not correspond to any set of lines on the first film. Thus we observe a total of four modifications in these two samples.

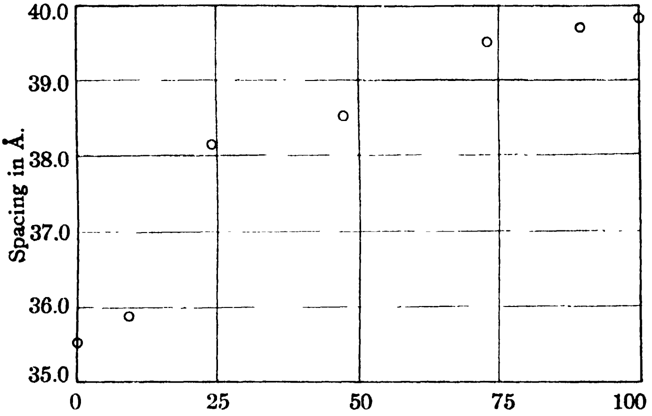


Graph II.—Mixtures of C_{10}–C_{12} acids.

(c) **Non-equimolar Mixture, Mole % C_{10} = 75.5; Mole % C_{13} = 24.5.**—A single picture was taken of the mixture. The calculations gave d = 24.64 Å. Only one set of lines is found for this mixture. The spacing obtained corresponds definitely to a mixed crystal and not to either pure acid.

For any of the three compositions listed above, mixed crystals are present since the spacings observed do not check with the pure acids. In the case of the mixture C_{10} = 75.5% and C_{13} = 24.5%, there is evidently complete mixing since there is only one phase present. In the case of the mixture C_{10} = 24.8% and C_{13} = 75.2%, we obtain a maximum of four phases. These phases represent different modifications and not phases with different composition. This is demonstrated by the fact that upon slow crystallization we obtain three phases, one of which is identical with one of the two phases obtained by rapid cooling; whereas the other is a new phase. Since the spacing corresponding to this common phase is nearly the same as the A modification for pure C_{13} acid, one might think that perhaps C_{13} crystallized out separately, leaving behind a mixture richer in C_{10}. This appears unlikely for two reasons: first, increase of speed of crystallization ought to hinder the separation of C_{13}; however, the intensity of this spacing on a sample obtained by rapid cooling shows no decrease in intensity. As a matter of fact, we find that the remaining phase (the residual mixture) from the rapidly cooled sample is present in very small amounts. In comparison with the sample with slow cooling, the sample with rapid cooling would appear to show smaller amounts of mixed crystals, which is certainly contrary to any reasonable anticipation. Second, the comparable mixture (C_{10} = 75.5%; C_{13} = 24.5%) shows complete solid solution formation only.

In the equimolar mixture we have either two phases of different composition or two phases of identical composition in different modifications. We favor the latter viewpoint in consideration of the results obtained with other mixtures, such as C_{10}–C_{12}.



Graph III.—Mixtures of C_{16}–C_{18} acids.

In addition to the C_{10}–C_{13} mixtures studied above an equimolar mixture of C_{15} and C_{18} acids (C_{15} = 49.8%; C_{18} = 50.2%) was investigated. The calculations gave spacings of 39.76 and 37.31 Å.

It is seen that this mixture gives two spacings, the values of which lie approximately half-way between the values of the proper modifications of C_{15} and C_{18} pure acids.

5. Systems with Components which Are Four Carbon Atoms Apart.—An equimolar and a non-equimolar mixture of C_{10} and C_{14} acids were used for investigations of mixtures of acids of n and $n + 4$ carbon atoms apart. The results obtained were: (a) two pictures were taken of the equimolar mixture of C_{10} and C_{14} acids (C_{10} = 50.1%; C_{14} = 49.9%). The first picture was taken immediately after the sample plate was prepared (d = 26.98) and the second picture on the same sample after two weeks had elapsed (d = 31.19).

On film (1) there was an indication of a first order (too weak to measure) of another series of lines which would give a longer spacing than the 26.98 Å. which was observed. This longer spacing would in all probability correspond to the spacing calculated from film (2). On film (2) there was not even an indication of a set of lines corresponding to the 26.98 Å. spacing, which means that the transformation to the modification with the longer spacing was complete.

It is of interest to note that according to the average composition (C_{12}) we find the spacing in the first picture close to the C modification of pure C_{12} acid (the only modification observed for this acid). It has been observed in previous cases (C_{10}–C_{12} and C_{10}–C_{13} mixtures) that such mixtures upon standing, or upon variation in speed of solidification, will change modification. In the present case a change of spacing occurs which we would like to interpret in a similar fashion. However, the new spacing observed corresponds closely to the C modification of pure C_{14}. We therefore have to consider the possibility of an unmixing of our sample. Since our original mixture has to be considered as a random arrangement it is hard to imagine that chains possessing considerable length may rearrange to form crystals containing one chain length only. Such a rearrangement, which would involve the moving about of the chains in a relatively regular crystalline arrangement, is quite different from the type of change involved in a change of modification. There, only a variation in tilt is necessary which does not affect, fundamentally, the relative position of the chain-like molecules. This latter possibility can be easily imagined to occur, and experiments show that it does occur. The first possibility appears quite unlikely and the experimental evidence seems to be against it. Namely, since we have an equimolar mixture, the formation of crystals of pure C_{14} only would by necessity give rise to the formation of crystals of pure C_{10}. This C_{10} acid would be crystallized under the conditions of the experiment. In consideration of the smaller size of the C_{10} molecules, these crystals could be formed as readily as those of C_{14}. However, although we find a spacing close to that of pure C_{14}, we find absolutely no trace of spacings that might be associated with any modification of pure C_{10}. Furthermore, if unmixing in the solid would occur, one would not expect it to be complete; so that there would remain lines corresponding to the original mixture (or one similar to it), which is in no way indicated by experimental evidence. Also if the C_{14} acid that might be separated is entirely free of C_{10} acid, the spacing observed is sufficiently different from pure C_{14} acid as to be outside the experimental error. In the still clearer case of C_{14}–C_{18} acid mixture (the data on this mixture are given below) no indication of unmixing was found at all. Thus we feel justified in claiming that the C_{10}–C_{14} mixture does not unmix in the above case, and that the new spacing observed upon standing is a new modification of the original mixture, which by chance falls close to the C modification (the only modification observed) for pure C_{14}. We have emphasized this point because similar phenomena occur in many binary mixtures of components more than four carbon atoms apart. (b) The non-equimolar mixture of C_{10} and C_{14}(C_{10} = 25.0%; C_{14} = 75.0%) upon exposure gave a picture with just one set of strong lines. There were, however, three very faint first order reflections appearing in addition. The four modifications have the following spacings: 31.27 (strong), 33.88, 28.54 and 26.96. (c) An equimolar mixture of C_{18} and C_{14} (C_{18} = 50.1%; C_{14} = 49.9%) gave the two spacings 39.05 and 35.58 Å.

Since the equimolar mixture of C_{14} and C_{18} acids has a composition equal to pure C_{16} acid, it is of interest to compare the spacings obtained in each case. The spacing of 35.58 Å. corresponds very closely to the C modification of pure C_{16} acid (which value is 35.53 Å.). Only the C modification of pure C_{16} acid was observed by us. Francis, Piper and Malkin,[6] however, report a B modification for pure C_{16} acid with a spacing of 39.1 Å.

6. Systems with Components which Are Five Carbon Atoms Apart.—For the study of mixtures of chains of n and $n + 5$ carbon atoms an equimolar mixture of C_{10} and C_{15} acids was used. Two separate sample plates were prepared and exposed and the results obtained from each are given: mole % C_{10} = 50.1; mole % C_{15} = 49.9; d = 39.62, 35.35; 28.06 and 24.98; d = 39.70, 35.44 and 27.93.

We have four modifications for this equimolar mixture. This makes the interpretation somewhat difficult, especially in view of the fact that two of the spacings correspond closely to the A and B modifications of pure C_{15} acid. In view of our previous discussions we would be inclined to believe that such coincidences are accidental and consider all four phases as different modifications only. Whether this be true or not, it is quite definite that we have at least partial mixed crystal formation, since two of the phases present give a spacing which cannot be brought into agreement with any of the known data on either pure C_{10} or C_{15} acids.

7. Systems with Components which Are Six Carbon Atoms Apart.—Two equimolar mixtures were used for the study of mixtures of chains of n and $n + 6$ carbon atoms. (a) An equimolar mixture of C_{10} and C_{16} acids (C_{10} = 49.9%; C_{16} = 50.1%) gave spacings equal to 35.31 and 29.15 Å.

Here we see that there are two sets of lines observable; the 29.15 Å. value being very close to the value that C_{13} acid would have if it fell on the even acid curve. The value of 35.31 Å. may correspond to the A modification for pure C_{13} acid. This value as found by us was 34.92 Å. Francis, Piper and Malkin[6] report a value for the A modification of pure C_{13} acid of 35.3 Å. However, it is to be noticed that this value (35.31 Å.) is close to the C modification of C_{16} acid. In view of the previous discussion, we would be inclined to believe that this coincidence is accidental, which is strengthened by the fact that C_{13} acid (which is the average of an equimolar mixture of C_{10} and C_{16} acids) does have a spacing close to this value. At any rate it is quite definite that there exists at least partial solid solution formation, since the other spacing observed (29.15 Å.) does not correspond to any known spacing for pure C_{10} or pure C_{16} acids. Similar results are indicated by the equimolar mixture of C_{12} and C_{18} acids (C_{12} = 49.9%; C_{18} = 50.1%), the spacings of which were *d* = 33.32, 28.81, 39.41.

Here a total of three phases is observed. Since the spacings of 33.32 Å. and 28.81 Å. cannot be fitted with any known modifications of pure C_{12} or C_{18} acids, we are certain that at least partial solid solution exists. The spacing of 39.41 Å. corresponds closely to the C modification of pure C_{18} acid but it also corresponds closely to the A modification of pure C_{15} acid (the average composition of an equimolar mixture of C_{12} and C_{18} acids), so that in this case the mixed crystal formation may be almost complete.

8. Systems with Components which Are Eight Carbon Atoms Apart.—An equimolar mixture of C_{10} and C_{18} acids (C_{10} = 49.9%; C_{18} = 50.1%) gave the spacings 31.12, 39.62 and 23.14 Å.

Here we observe three phases, two of which may be identical with the spacings of pure C_{10} and pure C_{18} acids. However, there remains a third phase which has a spacing which cannot be brought into accord with any known spacing for pure C_{10} or pure C_{18} acids. It must therefore be a solid solution of C_{10} and C_{18} acids. So here, as in any previous case, we find at least partial mixed crystal formation.

II. Complex Mixtures of Fatty Acids

In view of the fact that mixed crystals were rather easily formed for two component mixtures of acids over a wide range, it seemed to us quite probable that mixed crystals could be formed for mixtures of more than two components. Francis, Piper and Malkin[6] have shown in their interesting paper that for three neighboring acids in the fatty acid series mixed crystals are easily formed and that from such mixtures a single spacing is obtained. They, however, do not extend their experiments to include more complex mixtures. We have extended such experiments to include mixtures of as many as nine components. Four of these complex mixtures were studied.

The samples and sample plates were prepared in the same manner as described for the two-component mixtures. In all of the pictures obtained from these complex mixtures only two orders (first and third) were observable for a particular phase. The lines were somewhat broadened and the time of exposure was longer than for the two-component mixtures.

The results obtained are as follows. (1) An equimolar mixture of the even acids from C_{10} to C_{18} was studied. Three pictures were taken of this sample. The actual composition was: C_{18} = 18.9%; C_{16} = 19.0%;

C_{14} = 19.5%; C_{12} = 20.2%; C_{10} = 22.4%. For the first and third order $\sin \Theta/n$ = 0.01969 (com.) and 0.01962; average = 0.01965; d = 39.15 Å. In another case $\sin \Theta/n$ = 0.01972 (com.) and 0.01963; average = 0.01967; d = 39.11 Å.

Here just a single spacing was observed indicating complete solid solution formation and the check obtained on the two pictures indicates the reproducibility of the results.

This mixture was also studied by depositing the sample on the glass plate by crystallization from an acetone solution of the mixture. The calculations obtained are as follows (again for the first and third order): $\sin \Theta/n$ = 0.01948 (com.) and 0.01940; average = 0.01944; d = 39.57 Å.

This picture gives one main spacing as calculated above. Also there are indicated several weak first orders of other series of lines, which appear as a band, and which correspond to spacings shorter than the one calculated, indicating partial unmixing as to be expected.

(2) An equimolar mixture of the odd acids from C_{11} to C_{17} was studied. Two pictures were taken; one picture from a sample which was prepared by rapid crystallization of the melt and the other from a sample which had slow crystallization. The actual composition of this mixture was: C_{17} = 26.4%; C_{15} = 25.3%; C_{13} = 24.0%; C_{11} = 24.3%.

(a) **Sample Prepared by Rapid Crystallization.**—For first and third order $\sin \Theta/n$ = 0.01951 (com.) and 0.01941; average = 0.01946; d = 39.53 Å.

(b) **Sample Prepared by Slow Crystallization.**—For first and third order $\sin \Theta/n$ = 0.01906 (com.) and 0.01901; average = 0.01903; d = 40.43 Å.; and first order of second modification $\sin \Theta$ = 0.02059; d = 37.36 Å.

In this second example where slow crystallization of the sample was used we see that the sample gave two spacings (the spacing 37.36 Å. being weak and appearing in the first order only), indicating that under these conditions we obtain either two modifications or the mixed crystal formation is not complete whereas in the first case certainly complete solid solution formation is present.

(3) An equimolar mixture of all of the acids from C_{10} to C_{18} inclusive was made up and the x-ray picture taken. The actual composition of this mixture was: C_{18} = 11.1%; C_{17} = 11.1%; C_{16} = 11.3%; C_{15} = 11.3%; C_{14} = 11.3%; C_{13} = 11.3%; C_{12} = 11.1%; C_{11} = 10.8%; C_{10} = 10.7%. From first and third order $\sin \Theta/n$ = 0.01944 (com.) and 0.01945; average = 0.01945; d = 39.55 Å.

Even with a mixture as complex as this one, only one spacing is observable, indicating that the mixed crystal formation must be essentially complete. (4) A non-equimolar mixture of the even fatty acids from C_{10} to C_{18} was studied. This mixture contained a larger percentage of the higher acids.

The actual composition was as follows: C_{18} = 29.8%; C_{16} = 29.2%; C_{14} = 19.6%; C_{12} = 10.4%; C_{10} = 11.0%. From first and third order $\sin \Theta/n$ = 0.01949 (com.) and 0.01945; average = 0.01947; d = 39.51 Å.

Discussion of Results

In the interesting paper by Francis, Piper and Malkin[6] the idea was put forward that the x-ray results on equimolar mixtures of fatty acids might best be explained by assuming an arrangement in which a short and a long molecule would form a double molecule. Since double layers of molecules exist in crystals of pure fatty acids, and since always the length associated with such double molecules is measured, such an arrangement would indeed furnish a simple explanation for the fact that the spacing obtained from the mixture is the mean of the spacings of the components (provided that the proper modifications are taken). We have been inclined to consider such an explanation not adequate, since it is hard to anticipate that from a melt of the mixture such a regular arrangement could be obtained upon rapid cooling. Furthermore, since the forces holding various such molecules together in the lattice are about the same, the difference in energy of an ordered and a non-ordered crystal is small.

The experimental test gives the best answer to these questions. The suggested arrangement can only be complete in equimolar mixtures. It is, therefore, of interest to study mixtures of various concentrations. This has been done for the C_{10}–C_{11} mixtures in which it was shown that for any and every composition one definite spacing was obtained, which spacing was characteristic for a particular mixture. When such spacings are plotted against the composition it is found that the points are scattered closely around the straight line connecting the pure acids (graph I). The fact that the equimolar mixture gives the mean spacing of the two components is therefore nothing more than a special case of this more general rule. Obviously the assumption of double molecules, which has occasionally been brought forward by other chemists, is untenable. These mixtures apparently follow the similar law known for inorganic solid solutions which is expressed approximately as Vegard's rule. It is not surprising that the values are relatively widely scattered, since it has become evident in the previous discussion of the pure fatty acids that the spacings are easily affected by various influences. Similar results appear to be present in mixtures of C_{10}–C_{12} and C_{16}–C_{18}; however, in these cases the picture is complicated by the fact that various compositions do not correspond to the same modification. It appears as if two to three modifications were present, so that the points are scattered around two or three lines, one of which connects the spacings of the pure components. Similar results are obtained for the C_{10}–C_{18} mixtures. In this connection attention must be called to a recent paper[7] in which the existence of a transition point for

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(7) R. L. Shriner, J. M. Fulton and D. Burks, THIS JOURNAL, 55, 1494 (1933).

mixtures of palmitic and stearic acid is interpreted as proof for the formation of a compound. Contrary to this view we are inclined to assume a change in modification only.

Francis, Piper and Malkin[6] indicated that solid solution does not exist in binary mixtures in which the chain length difference is more than three carbon atoms. However, we have obtained definite solid solution formation with C_{10} and C_{14} acids in two concentrations and for one concentration of C_{14} and C_{18} acids (no other concentrations were investigated). In the case of five, six and eight carbons apart it was definitely proved that at least partial solution exists in the solid state. Such mixtures had always C_{10} acid as one component, thus giving a relatively high percentage difference in chain length.

It is of interest to note that the mixtures appear to occur in a larger number of modifications than has been observed for the pure acids in this investigation.

It is a remarkable fact that for any one of the complex mixtures listed in the experimental part, a definite single spacing characteristic for one phase can be obtained. Since one phase only is obtained, this must mean that complete solid solution is present in these cases.

It is likely that the modification present in such mixtures corresponds to the one present in certain binary mixtures with large separation of chain length, namely, the ones which give the longest spacing. This may be surmised from the fact that in the case of these complex mixtures the spacing lies close to the one of the longest component. However, it must be emphasized again that this similarity of spacing cannot mean that the highest component has crystallized out, since definitely no other spacings are present in the proper samples.

In the sample which has been obtained from solution a partial separation has been observed. The spacing is slightly longer than the one obtained from the corresponding melt. Assuming identical modifications, this would mean that the main component contains more of the longer chains than would be given by the average composition, which again would necessitate the presence of phases with a higher content of the lower chains. Actually the main spacing is accompanied by a narrow weak band which must have been produced by various slightly shorter spacings.

The fact that such complex but well-defined mixtures of fatty acids give rise to well-defined reflections from the (001) plane, which interplanar distance must be associated with the chain length (although in the case of the fatty acids, due to the unknown tilt of the chains, the average chain length cannot be definitely calculated), is of special interest, since in previous investigations such an effect was claimed not to exist. Hengstenberg[8] was unable to obtain any spacings associated with the chain length

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(8) J. Hengstenberg, *Z. Krist.*, **67**, 538 (1928).

in a complex hydrocarbon mixture (the average length is not given in the reference, but judging from the title the paraffin mixture may be assumed to be C_{60}–C_{80}).

It might be argued that the average chain length was too high to be observable. With our apparatus, depending on the third order which is sufficiently strongly observed in our mixtures, we could measure spacings for a hydrocarbon mixture of average chain length of about C_{100}. It might be objected that the results obtained on the fatty acids are not applicable to other long-chain compounds. For this reason other series are being investigated. At present the preliminary results are available on several series, for which Dr. D. A. Wilson[9] observes the same effect. Since such perfect miscibility is observed for relatively short chain lengths, where the relative length differences of neighbors play a much larger role, it is reasonable to expect similar miscibility for longer chain lengths. Unfortunately such longer acids were not at our disposal in sufficiently pure form that the experimental test could be performed.

The results obtained on the mixtures of the acids are entirely nonambiguous in their interpretation. The lines obtained are surprisingly sharp although less sharp than those obtained on the pure acids or simple mixtures. The falling off of intensities with the higher orders appears to be more rapid than in the case of the pure acids. Since these findings are so much in opposition to the prevailing opinion[10] it seems of interest to make theoretical calculations on such mixtures. This has been done by Dr. M. L. Huggins[11] in this Laboratory. His results are in perfect agreement with our experimental data.

The results obtained seem to us to be of special interest in connection with the structure of high polymers. Some such polymers are assumed to consist of chains of various lengths. If the average chain length is not excessively long, spacings connected with this average chain length should be obtained by the methods used in this work. Such effects have not been previously observed, and this has been used thus far by other workers as a criterion for the presence of chains of varying length. There is only one dissenting paper[12] in which reflections were obtained from polymer formaldehydes which were considered as lower orders of the (001) plane; since the chains are vertical to the (001) plane, the average chain length could be calculated from the data. However, at the time instead of using the concept of average chain length it seemed more cautious to consider the crystals as built up of molecules of essentially the same length only, in agreement with the prevailing opinion. Since it was more likely from chemical considerations to assume varying chain length in polymer form-

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(9) Dissertation, the Johns Hopkins University, 1933.

(10) K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, 1930, pp. 44–45.

(11) Huggins, to be published shortly.

(12) Emil Ott, *Z. physik. Chem.*, **B9**, 378 (1930).

aldehydes, Sauter[13] attacks the existence of "inner" reflections (lower orders of the (001) plane) observed by Ott. In consideration of the results obtained in this thesis, there appears to be every reason to anticipate results such as obtained by Ott on polymer formaldehydes, since the spacings observed lie in a range suitable for observation.

Summary

1. A large number of two-component mixtures of the normal fatty acids C_{10} to C_{18} have been studied. The chain length difference of the two components varied from one to eight carbon atoms. The mixtures with difference in chain length up to three carbon atoms were studied for various concentrations. In all cases mixed crystal formation was established.

2. Very complex mixtures of fatty acids (containing as many as nine components) were also measured and the existence of solid solution demonstrated.

3. These results are discussed in connection with their chemical significance.

[13] E. Sauter, *Z. physik. Chem.*, **B18**, 417 (1932).

BALTIMORE, MARYLAND RECEIVED JUNE 8, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Heat Capacities of Gaseous Mono- and Dimethylamine[1]

BY W. A. FELSING AND F. W. JESSEN

Object of the Investigation.—The purpose of this investigation was the experimental determination of the heat capacities of mono- and dimethylamine in the gaseous state. This study is a continuation of a series by Felsing and co-workers[2] dealing with the thermodynamic constants of monomethylamine with a view to the possible use of this substance as the refrigerating fluid in the absorption type of refrigerating units. The inclusion of dimethylamine in this study serves to present, also for the first time, heat capacity data for this substance, which itself presents possibilities as a refrigerating fluid. A study of the thermal decomposition of the methylamines yields data at elevated temperatures leading to the evaluation of their free energies of formation from the elements. Such experiments, to be reported in a later paper, have been made; to evaluate the free energy content at 25°, however, requires a knowledge of the heat capacities of these gaseous amines. These data, hence, form the objectives of this investigation.

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[1] From a portion of a thesis submitted by F. W. Jessen in partial fulfilment of the requirements for the Ph.D. degree.

[2] Felsing and Thomas, *J. Ind. Eng. Chem.*, **21**, 1269 (1929); Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); C. T. Ashby, M. A. Thesis, University of Texas, 1931.

Previous Investigations.—The literature records no data for the heat capacities of the methylamines as gases. Planck and Vahl[3] cite a single value for the heat capacity of *liquid* monomethylamine at 20° and Vahl[4] cites one at 15°.

The Method of this Investigation.—The method best suited for an accurate determination of the heat capacities of substances such as the amines seemed to be the closed system continuous flow method of Scheel and Heuse.[5] This method was adopted, accordingly, utilizing such modifications as suggested by Thayer and Stegman and by Haas and Stegman.[6] Some minor modifications were made during this investigation. Special attention was paid to the very exact temperature control of the thermostat in which the calorimeter was immersed (*i. e.*, ±0.005°).

The Calorimeter.—The calorimeter in design followed that of Scheel and Heuse in general and was constructed of Pyrex glass. The heating unit was made of 300 cm. of double silk-covered manganin wire wound on a small glass tube, shellacked to ensure complete insulation. The brass tube T (see figure) was machined to fit the glass tube F of the calorimeter, inside of which it was placed and to which it was attached by means of de Khotinsky cement. The copper tube E was closed at its lower end by means of a fine copper gauze, soldered on. The space between the inner walls of this tube and the heater coil was packed with finely shredded copper, B, to ensure adequate thermal contact of the gas with the heater unit. The resistance of the heater unit was found to be 109.30 ohms, determined potentiometrically against a 10-ohm standard resistance calibrated by the U. S. Bureau of Standards.

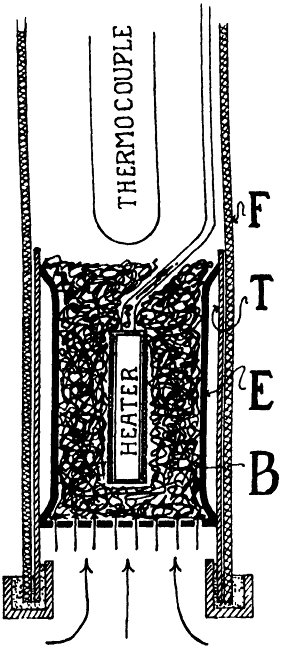

Fig. 1.—Details of calorimeter unit.

The Thermoelements.—All temperature measurements were made with a 15-junction copper–nickel thermoelement constructed according to the recommendations of La Mer and Robertson.[7] Although Tsutui[8] questions the dependability of the copper–nickel junction, it was found in this investigation that the calibration at different times gave identical results. A 10-junction copper–constantan element was constructed to check against the copper–nickel element. The thermoelements were 86 cm. long; the ends were staggered to avoid undue bulking. Both the cold and hot junctions were encased in a very thin-walled (0.15 mm. thickness) seamless silver tube, closed at one end and having a total length of 15 cm. Naphthalene was used to ensure good thermal contact of the junctions with the silver sheath. The calibrated thermoelements were used differentially to measure the temperature differences of the gas before entering and after leaving the heating unit.

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(3) Planck and Vahl, *Fortschr. Geb. Ingenierw.*, [A] **2**, 11 (1931).

(4) Vahl, *Z. Ges. Kälte-Ind.*, **38**, 177 (1931); **39**, 7 (1932).

(5) Scheel and Heuse, (a) *Ann. Physik*, **37**, 79 (1912); (b) **40**, 473 (1913).

(6) (a) Thayer and Stegman, *J. Phys. Chem.*, **35**, 1505 (1931); (b) Haas and Stegman, *ibid.*, **36**, 2127 (1932).

(7) La Mer and Robertson, *ibid.*, **35**, 1953 (1931).

(8) Tsutui, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **11**, 93 (1929).

Calibration of the Apparatus.—The apparatus was highly evacuated for six to eight hours before filling with pure air (moisture and carbon dioxide free). The specific heat of the gas was calculated by the relation, also used by Thayer and Stegman

$$\tilde{C}_p\,(\text{watt-sec./g.}) = (E/M\Delta T)\,[1 - K/M^2]$$

where E is the energy input in watts, M is the mass of gas passing through the heater unit per second, ΔT is the temperature rise, and K is the heat loss constant of the calorimeter. The value of K was determined in the usual way by varying the rate of flow of the gas and the heat input to maintain a constant temperature rise. The value of K for this apparatus for air was found to be 4.92×10^{-5}. The molal heat capacity of air at 25° was found in this investigation to be 6.960 cal./mole, which value is in excellent agreement with recent determinations of Scheel and Heuse,[5b] of Grüneisen and Merkel,[9] of Hebb,[10] of Shields[11] and of Thayer and Stegman.[6b]

The Heat Capacities of Mono- and Dimethylamine Gases.—Monomethylamine and dimethylamine gases were generated by the action of 40% potassium hydroxide on their highly purified hydrochlorides. The gases were dried by passage through long tubes filled with potassium hydroxide pellets and they were condensed in a reservoir surrounded by a mush of carbon dioxide and ether. After evacuation they were distilled from the reservoir, now surrounded by an ice–salt mixture, into another reservoir surrounded by the carbon dioxide–ether mush. Only about two-thirds of the liquid in each case was thus distilled into the new reservoir. This procedure was repeated several times to ensure a pure, dry product. The final product was then passed as a gas into the closed heat capacity system.

The heat capacities were determined at temperatures ranging from 0 to 50°. Table I presents the data obtained for both mono- and dimethylamine. These heat capacity data were plotted to large scale and the values of C_p determined as functions of the temperature. The following relations were obtained, which may be expected to determine the molal heat capacities even to temperatures considerably higher than the experimental limit of 50°.

$$\tilde{C}_p\ \mathrm{CH_3NH_2}\ (\text{g.})\ (\text{cal./mole}) = 9.530 + 0.1108T - 1.212 \times 10^{-4}T^2$$

and

$$\tilde{C}_p\ \mathrm{(CH_3)_2NH}\ (\text{g.})\ (\text{cal./mole}) = 5.595 - 0.1148T + 2.750 \times 10^{-4}T^2$$

The Heat Capacity Ratios.—It seemed desirable to determine also the heat capacity ratios for these amines, specially since no such data for them are recorded in the literature. The method adopted was that of Kundt,[12] as modified by Saha.[13] Some modifications in connection with the production of sound were also introduced. At one end of the gas tube a telephone receiver connected to a variable high frequency vacuum tube oscillator, as described by Oldfather,[14] served as the source of sound. The receiver was placed inside a machined brass fitting, a special graphitic packing being employed to secure a gas-tight joint between the glass tube and the coupling enclosing the telephone receiver. The remainder of the

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(9) Grüneisen and Merkel, *Ann. Physik.*, [4] **72**, 193 (1923).

(10) Hebb, *Trans. Roy. Soc. Canada*, [3] **13**, 101 (1919).

(11) Shields, *Phys. Rev.*, **10**, 525 (1917).

(12) Kundt, *Pogg. Ann.*, **127**, 497 (1866); **135**, 337, 527 (1868).

(13) Saha, *Indian J. Phys.*, **6**, 445 (1931).

(14) Grace Oldfather, M. A. Thesis, University of Texas, 1929.

TABLE I

THE HEAT CAPACITIES OF MONO- AND DIMETHYLAMINE GASES

T, °C.	ΔT, °C.	M (g. gas/sec.)	E (watts) (RI^2)	K ($\times 10^4$)	C_p watt-sec/g.	C_p cal./mole
		I. Monomethylamine				
0	5.3550	0.01280	0.15780	0.492	1.6110	11.97
	5.4862	.01249	.15780	.492	1.5770	11.72
	5.5788	.01271	.15780	.492	1.5462	11.48
					Average	11.72
25	5.4876	.01232	.17500	.492	1.7485	12.98
	5.3255	.01093	.17500	.492	1.7700	13.14
	5.6402	.01248	.17500	.492	1.6992	12.62
					Average	12.91
50	5.4720	.01049	.19264	.492	1.8528	13.76
	5.8815	.00936	.19264	.492	1.8450	13.69
	5.3785	.01248	.19264	.492	1.8760	13.92
					Average	13.79
		II. Dimethylamine				
10	4.3430	0.01440	0.11920	0.471	1.4685	15.802
12	4.3350	.01413	.11920	.471	1.4850	15.975
25	4.5620	.01634	.14175	.471	1.5670	16.870
	4.5784	.01705	.14175	.471	1.5225	16.380
					Average	16.575
40	4.8355	.01241	.14175	.471	1.6750	18.030
50	4.9986	.01324	.15780	.471	1.7450	18.770
	4.9942	.01378	.15780	.471	1.7230	18.550

apparatus and its operation involved no new features. All determinations were carried out at 25° in a specially constructed thermostat.

The procedure of a determination involved the evacuation of the apparatus to pressures less than 0.001 mm., filling with pure, dry air, setting the oscillator at a definite constant frequency, and determining the nodal distances. After evacuating as before, pure, dry amine was admitted and, with the identical oscillator frequency, the nodal distances were again determined. The values for the ratio, γ, were calculated by the usual relation $\gamma = 1.403(M/29.0)(l_2^2/l_1^2)$, where 1.403 is the value of γ for air; 29.0 is the molal weight of air; M is the molecular weight of the amine; and l_1 and l_2 are the experimentally determined nodal distances for air and the amine, respectively.

TABLE II

THE HEAT CAPACITY RATIOS OF SEVERAL AMINES AT 25°

Substance	CH_3NH_2[15]	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$[15]
$\gamma = C_p/C_v$	1.202	1.149	1.184	1.135

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(15) Since this paper was submitted for publication, Mehl [*Beihefte Z. ges. Kälte-Ind.*, Reihe 1, Heft 3 (1933)] published a value for $\gamma = 1.18 \pm 0.01$ for CH_3NH_2 (p. 27) and $\gamma = 1.13 \pm 0.01$ for $C_2H_5NH_2$ (p. 20).

The calculated values are listed in Table II; values for trimethylamine and monoethylamine are also included.

Summary

1. The need for heat capacity data for the amines and the absence of such data in the literature are pointed out.

2. Experimental values for heat capacities are presented tabularly and the heat capacity–temperature relations for the mono- and dimethylamines are presented for a temperature range from 0 to 50°. The accuracy of the measurements is given.

3. Experimental values for the heat capacity ratio, γ, are presented for the methylamines and for monoethylamine.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 313]

The Conductance of Bases in Liquid Ammonia

BY WILLIAM W. HAWES[1]

I. Introduction

It is well known that a molecular species which consists principally of an element of the second period differs markedly in its physical and chemical properties generally when compared with its analogs of the succeeding periods. That the same trend would be shown if the species under consideration were ionic seems likely and we would expect the electrolytic conductance of solutions of a compound of this type to show an abrupt change from the behavior of the commoner types of electrolytic solutions. The evidence in support of this hypothesis is meager but examination of the available data does show discontinuities that are probably characteristic of the second period elements. However, the specific effect is usually involved and is, therefore, difficult of generalization.

Perhaps the approach to the problem most likely of success is a comparative study of dissociation of electrolytes consisting of the simplest ions of second period elements. This would necessarily have to be carried out in a solvent of dielectric constant sufficiently low that its solutions of ordinary electrolytes would be measurably undissociated. Unfortunately, this field of investigation is very restricted because such compounds are ordinarily insoluble in suitable media. The only systems that are readily available are the alkali metal amides in solution in liquid ammonia. Ammonia is well suited to this purpose since no electrolyte as far as is known at present is completely dissociated in this solvent and also, the conductance values of a large variety of electrolytes are available for comparison.

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[1] National Research Fellow in Chemistry.

The conductance of solutions of sodium and potassium amides in liquid ammonia was measured by Franklin and Kraus[2] and by Franklin. Two significant facts are shown by these data; first, both electrolytes are exceptionally weak and, second, the order of their relative strength is reversed, that is, whereas sodium salts generally are more highly dissociated than potassium salts, the dissociation of sodium amide is much less than that of potassium amide. It has been shown by Kraus and Hawes[3] that the dissociation of an electrolyte is primarily determined by the size and configuration of its ions. The amide ion is undoubtedly small and therefore these amides would be weak. While this characteristic is thus, qualitatively, accounted for there is no ready explanation of the great difference in the dissociation of the two nor of the relative order of their constants. In addition, the unusual properties of these amides are clearly demonstrated by their reactivity. The most striking example is, perhaps, the formation of compounds, stable even in solution, between these amides and between them and amides of the other strongly electropositive first group elements.[4] In view, then, of the known properties of the amides it seemed likely that more precise data might yield additional knowledge concerning the behavior of second-period elements. In the present paper are reported new determinations of the conductance of these solutions in which the concentration range is extended and the values somewhat revised. Also, evidence is presented of additional anomalous behavior that cannot be accounted for on the basis of existing theory.

II. Apparatus and Materials

The apparatus employed, exclusive of electrical equipment, and the general procedure adopted in this investigation were the same as was developed by Kraus and Hawes[3] in the measurement of the conductance of ammonia solutions of substituted alkali metal amides. Electrical apparatus comprising an alternating current bridge assembly was constructed according to current notions of design, following largely the recommendations of Shedlovsky[5] but incorporating some of the suggestions of Jones and Josephs.[6]

Apparatus.—The bridge assembly consisted of a bridge proper, two resistance boxes, a vacuum tube oscillator and a detector. The bridge was an equal ratio arm instrument consisting in the main of coaxially mounted woven coils of 1000 ohms each and fine adjustments of 14K white gold wire on both the ratio arm branch and the resistance-cell branch. Coarse and fine adjustment variable air condensers were provided for continuous variation of capacity from 500 $\mu\mu$f in parallel with the unknown to the same capacity in parallel with the reference resistances. Grounding was accomplished by means of a Wagner ground. The resistance boxes had a combined resistance of 60,000 ohms variable in steps of 0.1 ohm. Coils up to 100 ohms were bifilar wound while those of 1000 and 10,000 ohms were of the woven type. All coils were so spaced that sensible interaction between them was eliminated. Also, the 10,000-

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[2] Franklin and Kraus, *Am. Chem. J.*, **23**, 292 (1900); Franklin, *Z. physik. Chem.*, **69**, 290 (1909).

[3] Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933).

[4] Franklin, *J. Phys. Chem.*, **23**, 36 (1919).

[5] Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

[6] Jones and Josephs, *ibid.*, **50**, 1049 (1928).

ohm coils were arranged so that they were completely disconnected when not in actual use. They were oil immersed and thermostated. The absolute values of the resistances were determined by comparison with Bureau of Standards calibrated coils using direct current. The oscillator was of the type described by Shedlovsky and was designed to give frequencies from about 1000 cycles per second upward in convenient steps throughout the audible range. The data given below were obtained, using a single frequency of 1000 cycles per second but higher frequencies were used as well in checking possible frequency dependence in the resistance measurements. The oscillator was coupled to the bridge circuit through a variable air transformer. The detector consisted of a single high resistance telephone used in conjunction with a two-stage, transformer coupled, vacuum tube amplifier. The characteristics of the amplifier were such that a peak amplification was given in the neighborhood of 1000 cycles with considerable attenuation of lower frequencies. Attenuation of the higher frequencies was less pronounced so that bridge settings of the required accuracy could be made up to 5000 cycles. Each of the units of the assembly was shielded electrostatically as completely as possible except the oscillator, of which the output coil only was shielded. The shielding was well removed from current-carrying parts of the assembly. All external electrical connections were made through shielded single conductor copper wire, insulated by an extra heavy rubber covering of very low dielectric constant.

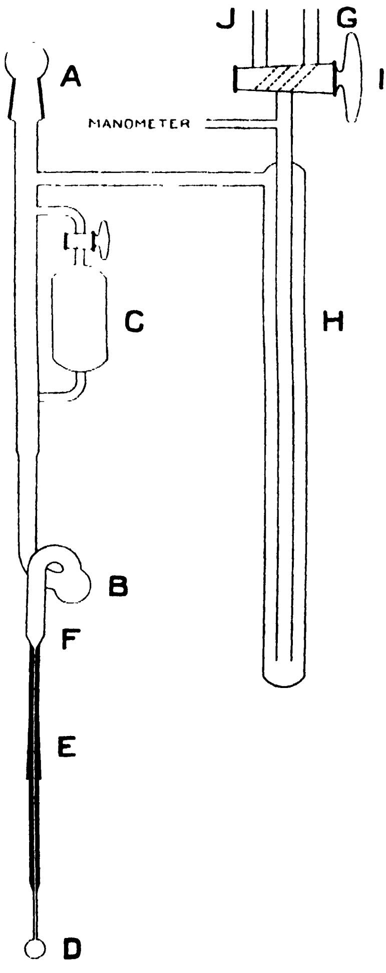

Fig. 1.

Materials.—The metal amides were prepared in the conductivity cell by the interaction of ammonia and a known quantity of the metal in the presence of oxidized iron. The cell having been washed repeatedly with pure ammonia until its specific resistance was sufficiently high, a fragile glass bulb containing the metal was crushed and the reaction allowed to proceed to completion. In the case of potassium this required only a few minutes but a much longer time was required for sodium, the time ranging from two or three days to a week. After the reaction was complete the solvent was evaporated without boiling, a stoppered Dewar tube being kept around the cell. This procedure was necessary to ensure complete retention of the amide. Hydrogen resulting from the reaction was removed by evacuation.

The metals were purified by distillation in the apparatus shown in Fig. 1. A commercial metal was introduced through the top A into the bulb B. The reservoir C was filled with nitrogen and closed off by the stopcock. The nitrogen was a commercial grade from which oxygen had been removed by passage over hot reduced copper and which had been stored over phosphorus pentoxide long enough to ensure complete drying. The weighed fragile bulb D was attached to the distilling apparatus through the capillary ground joint E, sealed internally with de Khotinsky cement on the outer end only. A tubular electric resistance furnace was placed in such a position around the distilling apparatus that a part of the metal was distilled from the bulb B to the top of the capillary F. The system (with the exception of the nitrogen reservoir) was evacuated continually during distillation by means of a diffusion pump connected at G, being protected from back diffusion of mercury by the trap H which was surrounded with liquid air. After the desired amount was collected at F the stopcock I was closed, the furnace removed and an oil-bath placed so as to immerse the fragile bulb and connecting tube to a height somewhat above the distilled metal. Maintaining the temperature of the bath slightly above the melting point of the metal, nitrogen was introduced from the reservoir C forcing the molten metal through the capillary into the bulb D. Sufficient additional nitrogen was then introduced from a storage flask attached at J to bring the pressure to within a few millimeters of atmospheric pressure. Removing the bath and allowing time for thermal equilibrium, the pressure and temperature of nitrogen were observed, after which the fragile bulb was sealed off. The lower half of the ground joint E was removed and weighed together with the bulb. After taking into account necessary corrections, the weight of metal was given by difference. The apparatus was constructed of soda lime glass, this glass being less readily attacked by the vapors of sodium and potassium than other common glasses.

A micro balance sensitive to 0.001 mg. was employed to weigh the samples of metal. Platinum weights intercompared by the Richards method[7] and checked at intervals throughout the range of the set against Bureau of Standards calibrated Class "A" weights were used. The principal correction to the observed weight was made necessary by the volume of air displaced by metal and nitrogen. This was determined by weighing the bulb under water on an analytical balance. All corrections significant to 0.001 mg. were taken into account. The weights of metal recorded below may be relied upon probably to 0.005 mg.

The ammonia was a synthetic product dried by sodium and stored in a metal cylinder from which it was distilled as needed. The vapor was passed through a filter of washed and ignited asbestos. The specific conductance of the ammonia in the conductivity cell was found to be about 1×10^{-7} and the data here given are corrected by this amount.

III. Experimental Results

Below are tabulated the conductance values at various dilutions for sodium amide, $NaNH_2$, and potassium amide, KNH_2. At the head of each table are given the temperature at which the measurements were made and the weight of metal used. Other data in the case of potassium amide were obtained, especially over the more concentrated range, which are in good agreement with the data given here but which are omitted for economy of space. V is the dilution in liters per equivalent and Λ the equivalent conductance in the usual units.

TABLE I

CONDUCTANCE VALUES OF BASES IN AMMONIA

Temp., −33.04°. Sodium Amide. Na, 0.01368_1 g.

V	Λ	V	Λ	V	Λ
72.48	10.24	272.7	21.90	1024	41.35
140.7	15.28	528.8	30.47	1986	55.20

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(7) Richards, THIS JOURNAL, **22**, 144 (1900).

TABLE I (*Concluded*)

V	Λ	*V*	Λ	*V*	Λ
		Temp., −33.01°. Na, 0.010195 g.			
97.43	12.20	1351	47.64	18,760	137.8
189.7	17.81	2607	63.92	36,210	168.3
366.2	25.29	5022	84.57	...	...
703.6	35.00	9727	109.5	...	...
	Temp., −33.01°. Potassium Amide. K, 0.063529 g.				
17.61	19.00	495.1	66.93	13,660	208.1
34.36	23.36	963.2	88.32	26,590	230.8
67.18	29.82	1871	113.3	51,720	253.4
130.7	38.82	3650	143.6	...	...
254.1	50.95	7087	176.2	...	...
		Temp., −32.95°. K, 0.134012 g.			
8.37	16.12	230.7	49.25	6,374	173.5
16.25	18.61	447.5	64.66	12,400	204.2
31.56	22.73	868.1	84.79	24,130	228.3
61.01	28.84	1688	110.0	47,020	255.3
118.7	37.48	3283	140.1	...	...

IV. Discussion

The results for sodium and potassium amide are shown graphically in Fig. 2, in which the equivalent conductance is plotted as a function of the logarithm of the dilution. Only one of the sets of data given is plotted in each case. The data not plotted fall on the curve shown practically as well as those which are plotted except, possibly, in the most dilute region where the experimental uncertainty becomes relatively larger and since the points of check determinations tend to cluster they are omitted to avoid confusion. It is apparent that in both cases the equivalent conductance varies but little with concentration in the concentrated region but rises rapidly in the moderately dilute range, indicating a high value of the limiting conductance. A minimum in the curve for potassium amide exists at a concentration slightly higher than the range of these measurements. There is no minimum in the sodium amide curve but it may be inferred that the effect which produces the minimum in the potassium amide curve is present here also. This minimum is accounted for in solvents of very low dielectric constant by the hypothesis of ion triples.[8] It may well be that the same situation obtains here but no method of analysis is available to separate the effect precisely. Even so, it is obvious that both these electrolytes are extremely weak.[9]

Errors are present in the data for sodium amide of both Franklin and Kraus[10] and Franklin.[11] Franklin reports the conductance up to concentra-

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(8) Fuoss and Kraus, THIS JOURNAL, 55, 2387 (1933).

(9) The primary effect of ion triples is to increase the conductance.

(10) Franklin and Kraus, *Am. Chem. J.*, 23, 292 (1900).

(11) Franklin, *Z. physik. Chem.*, 69, 290 (1909).

tions of 5.7 liters and Franklin and Kraus up to 27.5 liters. Moreover, these two sets of data do not agree over the range in which they overlap. In the concentration range that the present data cover, namely, down to 72.5 liters, the general shape of the curve is the same as that of Franklin and Kraus but it lies above by an amount corresponding to an error of around 7 or 8% assuming that the present data are substantially correct. The author has found it impossible to prepare solutions of sodium amide substantially more concentrated than those reported. No accurate determination was made of the limit of solubility but qualitative observations indicated that saturation would be attained at approximately 50 liters. The results of Franklin and Kraus could be explained on the assumption that undissolved salt was present in the first three solutions they report but that all of the salt was dissolved thereafter. Their first four points were determined without removal of solution so that any error due to this source would be limited to calculated concentrations greater than approximately 50 liters. From this point on their results would be correct except for an initial concentration error. The error that is found is in the direction that would be expected from the manner in which their salt was prepared. The present revision of these data is not large in absolute magnitude, the relatively high percentage error being due to the low value of the conductance in this concentration range. The results of Franklin are obviously in considerable

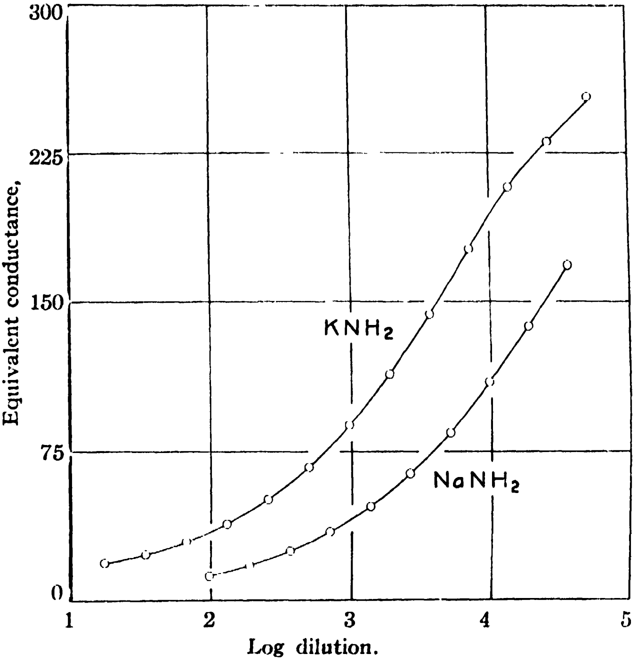

Fig. 2.

error. In his procedure the salt was made in an auxiliary cell and a solution siphoned to the measuring cell. The initial concentration would be far less than that reported so that subsequent concentrations and, of course, values of equivalent conductance, would be in error. The present data for potassium amide agree well with those of Franklin but are more consistent among themselves and also between separate series of measurements. Franklin's data fit the curve in Fig. 1 almost as well as any curve that might be drawn through them up to about 7500 liters. The present values of conductance are somewhat higher over this range of concentrations but the difference is within the experimental uncertainty of the earlier work.

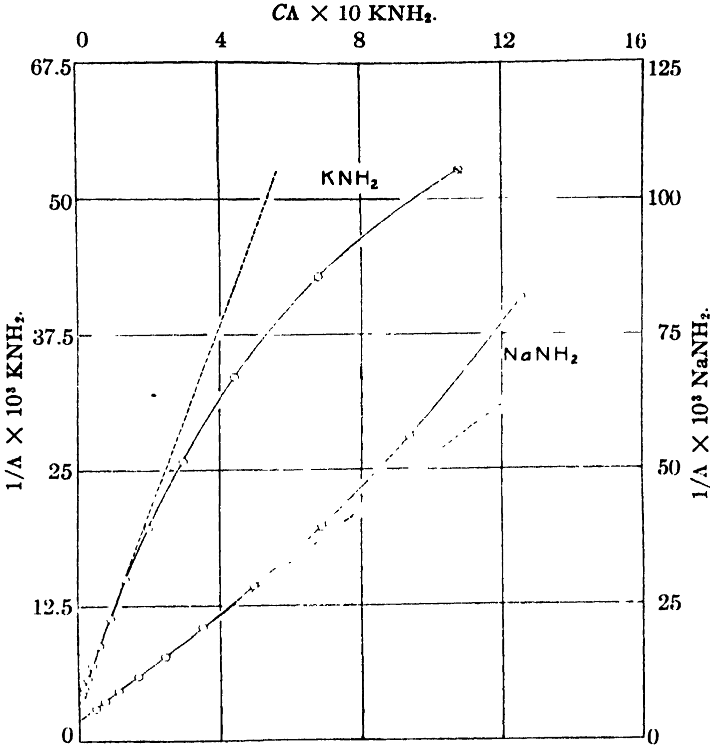

Fig. 3.

In Fig. 3 are plotted values of specific conductance (concentration times equivalent conductance) against the reciprocal of the equivalent conductance for a typical series each of measurements on sodium and potassium amide. It may be seen from these curves that both electrolytes apparently approach the law of mass action in the dilute region. The curve for potassium amide is normal and departs from linearity in the concentrated region in the manner that would be expected. Sodium amide, on the other hand, behaves quite differently. A pronounced curvature away from the axis of specific conductance is apparent. In other words, out to fairly dilute solutions sodium amide is a poorer conductor than is required by the law of mass action. This behavior is unique; no other salt as far as is known deviates in this manner.[12] The apparent agreement of the data with the Ostwald dilution law may be fictitious. Aside from the theoretical objection that no account is taken of the interaction of ions, the factors which are responsible for the abnormal curvature of the sodium amide curve might well compensate over a particular concentration range for the inaccuracies of the theory. The same effect may be entering with both electrolytes. Furthermore, extrapolation to zero concentration by this method yields values of Λ_0 almost identical for both the sodium and potassium amides.

An attempt to extrapolate these data for sodium amide by the method of Fuoss and Kraus[13] yielded no result. Their extrapolation requires that the plot of $f\sqrt{c}$ against $\gamma/\sqrt{1-\gamma}$ be a straight line passing through the origin. Here f is the activity, c the concentration and γ the degree of dissociation corrected for the interionic effect. This plot for sodium amide does not yield a straight line over any range of concentration and the direction of the deviation is again opposite to that found in every other case tried. It is not certain whether or not the data for potassium amide can be extrapolated by the method of Fuoss and Kraus. The curve shows a slight structure below 0.001 normal that is not readily explicable corresponding to conductance values progressively lower than predicted. It is not impossible that this is caused by a systematic experimental error. However, the deviations at the most dilute points are considerably greater than might be expected and are reproducible within much closer limits.

The only value of the dissociation constant of sodium amide that can be obtained at present is that given by the limiting slope of the curve shown in Fig. 3 assuming the simple mass action law (in the classical sense). The value so obtained, $K = 2.65 \times 10^{-5}$, is probably an upper limit for this constant. In the case of potassium amide, an extrapolation can be made by the Fuoss and Kraus method by disregarding the data below 4000 liters. The values so derived for the equivalent conductance at infinite dilution and the dissociation constant are $\Lambda_0 = 343$ and $K = 7.3 \times 10^{-5}$. Franklin's data extrapolate by this method to the values $\Lambda_0 = 351$ and $K = 7.0 \times 10^{-5}$. The simple mass action law gives $\Lambda_0 = 286$ and $K = 1.41 \times 10^{-4}$. The slope of the extrapolation curve in the Fuoss and Kraus

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(12) Kraus and Bray plotted this function for a large number of salts of widely differing dissociation constant some of which were of the same order of magnitude, and less than that of sodium amide, and in no case did they find a curve of this structure. Kraus and Bray, THIS JOURNAL, 35, 1315 (1913); Kraus, "The Properties of Electrically Conducting Systems," The Chemical Catalog Company, New York, 1922, pp. 55 ff.

(13) Fuoss and Kraus, THIS JOURNAL, 55, 476 (1933).

method which yields their determination of K seems to approach a much smaller limiting value than the simple mass action extrapolation in both cases.

In view of the failure of the theory to account for the conductance of sodium amide and the uncertainty of the treatment of potassium amide it would be useless to calculate ion sizes. If the underlying notions of the theory are at all justified it is certain, however, that the amide ion is exceedingly small. It may be that the unusual properties that have been found are specific for the amide ion but it seems more likely that they will prove rather to be characteristic of small ions in general.

V. Summary

The electrical conductance of sodium and potassium amide has been measured in liquid ammonia solution up to concentrations of 36,000 and 52,000 liters, respectively. The data for sodium amide deviate from the theory of Fuoss and Kraus as well as from the simple mass action theory. The agreement is better in the case of potassium amide but is not as good as might be desired. The results indicate that the specific properties of extremely small ions are important in the case of these electrolytes.

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The "Salting-out" and "Salting-in" of Weak Acids. I. The Activity Coefficients of the Molecules of Ortho, Meta and Para Chlorobenzoic Acids in Aqueous Salt Solutions[1]

BY ARTHUR OSOL AND MARTIN KILPATRICK

In general the solubility of a non-electrolyte is increased or decreased by the addition of an electrolyte, but the effect is not independent of the solvent salt. The results may be expressed by the equation

$$\log S_0/S = \log f \qquad (1)$$

where S_0 is the solubility at zero ion concentration, S the solubility in the salt solution and f the activity coefficient of the non-electrolyte. It has been found that the equation

$$\log f = kC \qquad (2)$$

C being the concentration of electrolyte in moles per liter and k a constant, holds over a wide range of concentration. The constant k is known as the "salting-out" constant. Provided a correction is made for the part present as ions, equation (2) is applicable to weak electrolytes also. In most of the early work on acids this correction was neglected, or improperly made, with the result that (2) did not hold.[2] It has been mentioned that for a given non-electrolyte the effect depends upon the solvent salt. It is also true that in general, for a given solvent salt, the effect depends upon the saturating non-electrolyte.[3] The "salting-out" constant *k* generally increases with decrease in the polar properties of the non-electrolyte. This is the basis of the theory of Debye.[4]

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(1) Abstracted from the dissertation of Arthur Osol presented April 1, 1933, to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy Paper presented in part before the Washington meeting of the American Chemical Society, March, 1933.

The theory of Debye does not explain how certain salts "salt-out" a specified non-electrolyte while others salt it in. An explanation has been offered by Kruyt and Robinson.[5]

The point of view of Kruyt and Robinson is briefly as follows. In a solution of a non-electrolyte in water, the water dipoles are arranged about a molecule of non-electrolyte with their positive or negative end toward the non-electrolyte depending upon the polar properties of the latter. When an electrolyte is added to the solution, due to the hydration of the ions less water is available to the saturating non-electrolyte and on this basis alone "salting-out" of the non-electrolyte is expected. There is, however, a counteracting effect. Its polar nature determines whether the molecule of non-electrolyte attracts cations or anions. About the attracted ions water molecules are arranged in a manner opposite to the arrangement about the non-electrolyte and the result of the approach of the ion to the molecule of non-electrolyte is a packing in of water molecules about the molecules of non-electrolyte, *i. e.*, "salting-in." The effectiveness of the specified ion depends according to Kruyt and Robinson upon its degree of hydration. The non-electrolyte is "salted-out" if the first effect predominates and *vice versa.*

This paper concerns the solubility of molecular ortho, meta and para-chlorobenzoic acids in various salt solutions and compares the "salting-out" constants obtained with those found for benzoic acid.

Experimental Part

The experimental method was that of Chase and Kilpatrick.[2] In order to minimize the correction for the part present as ions, buffer solutions were used throughout the work.

The chlorobenzoic acids were purified by recrystallization from alcohol. They melted sharply at 139, 154 and 235° for the ortho, meta and para acids, respectively. The criterion of purity was constancy of solubility upon repeated treatment of the solid with water. Titrations were carried out in an atmosphere of nitrogen with carbonate free sodium hydroxide. Weight burets were employed. When necessary the salts were purified by recrystallization.

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(2) Chase and Kilpatrick, THIS JOURNAL, **53**, 2589 (1931).

(3) Randall and Failey, *Chem. Rev.*, **4**, 291 (1927).

(4) Debye and McAulay, *Physik. Z.*, **26**, 22 (1925); Scatchard, THIS JOURNAL, **47**, 2069 (1925); *Chem. Rev.*, **3**, 383 (1927); Debye, *Z. physik. Chem.* (Cohen Festband), 56 (1927). For further references and a complete discussion see Falkenhagen, "Elektrolyte," S. Hirzel, Leipzig, 1933, p. 138–152.

(5) Kruyt and Robinson, *Proc. Acad. Amsterdam*, **29**, 1244 (1926). See also the very recent paper of P. M. Gross, *Chem. Rev.*, **13**, 91 (1933)

The total solubility of *o*-chlorobenzoic acid in water was found to be 0.01362 mole per liter. Correction for the part present as ions was made by multiplying the K_c/K_a ratio[6] for benzoic acid given by Chase and Kilpatrick by K_a for *o*-chlorobenzoic acid (1.28×10^{-3}) and applying the mass law to the K_c thus found to obtain the hydrogen-ion concentration. The corresponding solubility of the molecular acid is 0.00986 mole per liter. In a similar manner the total solubilities of meta and para chlorobenzoic acids were found to be 0.00246 and 0.000435 and the corresponding molecular solubilities 0.00191 and 0.000275. Table I gives the solubilities of the acids in dilute solutions of sodium salts of the acids.

TABLE I

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN SOLUTIONS OF THEIR SODIUM SALTS

o-Chlorobenzoic Acid

Sodium *o*-chlorobenzoate mole/liter	Density,[a] g. per cc.	Total acid mole per liter	H_3O^+, mole per liter	Molecular acid, mole per liter	$f = \frac{0.00990}{C_{o\text{HClB}}}$
0.01	0.997	0.01131	0.00135	0.00996	0.994
.02	.999	.01085	.00080	.01005	.985
.05	1.002	.01059	.00035	.01024	.967
.0962	1.003	.01075	.00021	.01054	.939
.20	1.011	.01135	.00012	.01123	.882

m-Chlorobenzoic Acid

Sodium *m*-chlorobenzoate					$f = \frac{0.00191}{C_{m\text{HClB}}}$
0.00212	0.997	0:00206	0.00014	0.00192	0.995

p-Chlorobenzoic Acid

Sodium *p*-chlorobenzoate					$f = \frac{0.000275}{C_{p\text{HClB}}}$
0.000342	0.997	0.000343	0.000065	0.000278	0.989

[a] The densities are given so that other workers can express the results in molality if that is preferred.

These results will be discussed in connection with the experiments on "salting-in." They are put in at this point to give the magnitude of the corrections in the experiments with the other salts given in Tables II to XI. It might be mentioned that the value for the solubility of *o*-chlorobenzoic acid at zero ion concentration, 0.00990 was obtained by the method of least squares for all the "salting-out" experiments (see Figs. 1 and 2). For *m*- and *p*-chlorobenzoic acids the corresponding values are 0.00191 and 0.00275.

Table II gives the results with potassium chloride. The values in column four were obtained as before with correction for the "salting-in" of the sodium salt.

The slopes of the potassium chloride lines in Figs. 1, 2 and 3 are equivalent to values of $k = 0.139, 0.142, 0.138$, respectively. The corresponding value for benzoic acid is 0.138.[2]

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(6) K_c represents the classical, K_a the thermodynamic, dissociation constant.

TABLE II

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN POTASSIUM CHLORIDE SOLUTIONS

KCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.1	1.002	0.01137	0.00961	0.128
.3	1.012	.01086	.00905	.130
.5	1.021	.01014	.00843	.139
1.0	1.042	.00861	.00719	.139
2.0	1.087	.00607	.00515	.142
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.007	0.00199	0.00179	0.147
.5	1.020	.00183	.00163	.136
.75	1.031	.00167	.00149	.143
1.0	1.042	.00158	.00141	.133
1.5	1.064	.00127	.00114	.148
p-Chlorobenzoic Acid				
Solutions 0.000342 molar in sodium salt. Correction = −0.000003				
0.5	1.020	0.000331	0.000238	0.129
1.0	1.041	.000273	.000197	.146
1.5	1.063	.000235	.000172	.136
2.0	1.086	.000206	.000153	.128
2.5	1.107	.000156	.000118	.147

TABLE III

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN SODIUM CHLORIDE SOLUTIONS

NaCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.005	0.01094	0.00915	0.171
.5	1.017	.00966	.00801	.182
2.0	1.076	.00498	.00422	.185
Solutions 0.02 molar in sodium salt. Correction = −0.00013				
0.5	1.018	0.00907	0.00806	0.179
1.0	1.039	.00739	.00658	.178
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.5	1.017	0.00174	0.00155	0.180
.75	1.027	.00156	.00140	.180
1.0	1.039	.00139	.00124	.187
2.0	1.076	.00094	.00085	.176

Table III gives the results with sodium chloride. Here and in all other cases the hydrogen-ion concentrations were calculated by combining the thermodynamic dissociation constant with the K_c/K_a ratios for each concentration of each salt as determined by Kilpatrick and Riesch by a catalytic method.[7] It seems reasonable to assume that the K_c/K_a ratios for the substituted benzoic acids are little different from the ratio for benzoic acid, in the given salt solution.[8]

Here and in Table IV it is shown that changing the buffer ratio makes no appreciable difference in the "salting-out" constant. In fact a comparison of the results for benzoic acid between buffered and unbuffered solutions showed that when proper corrections were applied the "salting-out" constants were the same in both cases. Studies in buffer solutions render the hydrogen-ion correction more certain.

The slopes of the lines for sodium chloride in Figs. 1 and 2 are 0.182 and

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(7) Kilpatrick and Riesch, unpublished results.

(8) Larsson and Adell, *Z. physik. Chem.*, **157**, 342 (1931).

0.180. Berry[2] as well as Güntelberg and Schiödt[9] find 0.176 for benzoic acid at 20°, while Larsson[10] gives 0.177 at 18° and from the results of Kolthoff and Bosch[11] for benzoic acid at 25° values ranging from 0.181 to 0.199 are calculated.

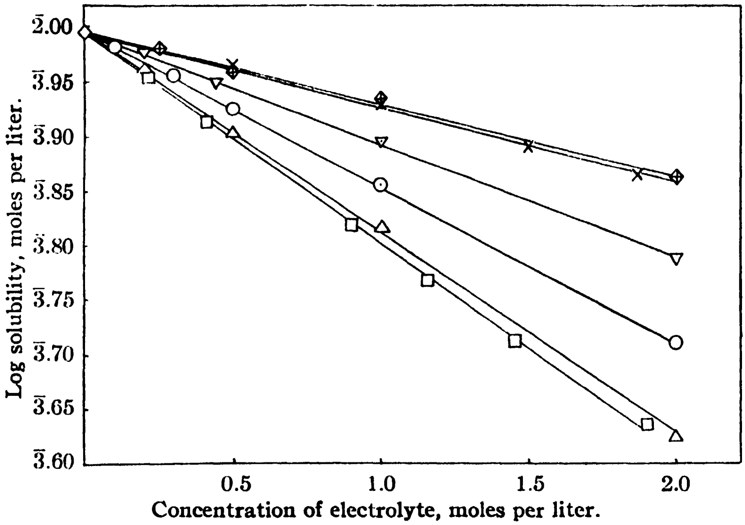

Fig. 1.—Solubilities of molecular *o*-chlorobenzoic acid in salt solutions: ×, $NaClO_4$; ▽, KBr; ○, KCl; △, NaCl; □, LiCl; ⊕, CsCl.

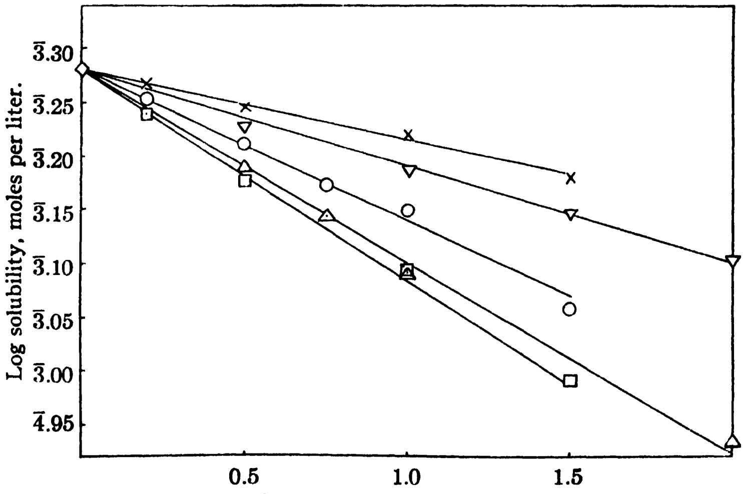

Fig. 2.—Solubilities of molecular *m*-chlorobenzoic acid in salt solutions: ×, $NaClO_4$; ○, KCl; △, NaCl; ▽, KBr; □, LiCl.

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(9) Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

(10) Larsson, *ibid.*, **153A**, 299 (1931).

(11) Kolthoff and Bosch, *J. Phys. Chem.*, **36**, 1685 (1932)..

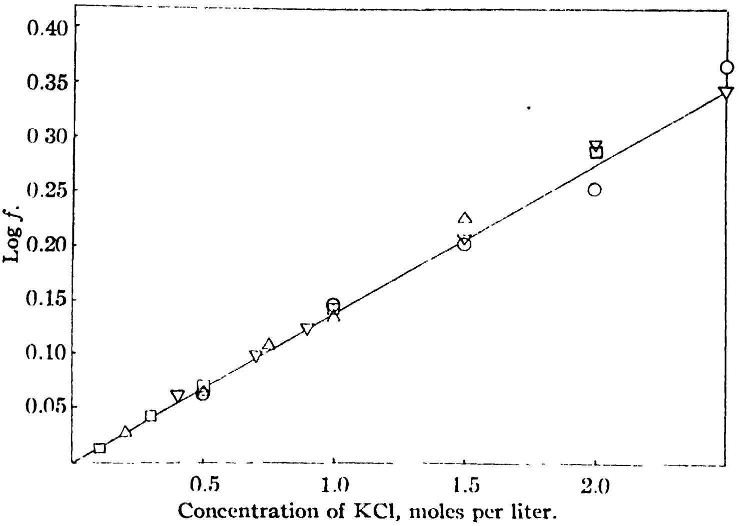

Fig. 3.—Activity coefficients of molecular benzoic, ortho, meta and para-chlorobenzoic acid in KCl solutions: ∇, benzoic; △, *m*-chlorobenzoic; □, *o*-chlorobenzoic; ○, *p*-chlorobenzoic.

TABLE IV

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN LITHIUM CHLORIDE SOLUTIONS

LiCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.988	1.022	0.00797	0.00642	0.190
1.157	1.026	.00731	.00588	.195
1.458	1.032	.00645	.00518	.193
1.905	1.045	.00529	.00433	.189
Solutions 0.02 molar in sodium salt. Correction = −0.00013				
0.213	1.004	0.01018	0.00902	0.190
.415	1.007	.00939	.00822	.194
.901	1.020	.00763	.00665	.192
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.003	0.00196	0.00174	0.207
.5	1.009	.00172	.00151	.200
1.0	1.021	.00143	.00125	.185
1.5	1.034	.00112	.00098	.192

TABLE V

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN POTASSIUM BROMIDE SOLUTIONS

KBr moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.017	0.01132	0.00949	0.091
.45	1.036	.01071	.00892	.100
1.0	1.083	.00943	.00789	.099
2.0	1.165	.00722	.00615	.103
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt Correction = −0.00001				
0.5	1.037	0.00190	0.00169	0.106
1.0	1.079	.00172	.00154	.093
1.5	1.121	.00156	.00140	.089
2.0	1.164	.00140	.00127	.089

The slopes of the lithium chloride lines in Figs. 1 and 2 are 0.193 and 0.193. Larsson finds for benzoic acid 0.192, while Kolthoff and Bosch give log f values from which constants may be obtained ranging from 0.186 to 0.213.

The slopes of the potassium bromide lines in Figs. 1 and 2 are 0.099 and 0.090. Larsson, reporting the solubilities of benzoic acid in three solutions, finds "salting-in" at the lowest concentration and gives the average value of k for the two others to be 0.070. Kolthoff and Bosch report activity coefficients which may be calculated to k values between 0.107 and 0.120. Haeseler's results are more complete and when corrected for the dissociated part give an average value of 0.113[12] at 25°.

TABLE VI

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN SODIUM PERCHLORATE SOLUTIONS

$NaClO_4$ moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.25	1.016	0.01152	0.00962	0.050
.50	1.038	.01096	.00922	.061
1.00	1.076	.00995	.00852	.065
1.50	1.113	.00895	.00781	.068
1.87	1.142	.00834	.00737	.068
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.012	0.00206	0.00185	0.064
.5	1.037	.00197	.00176	.067
1.0	1.075	.00183	.00166	.061
1.5	1.112	.00166	.00151	.069

TABLE VII

SOLUBILITIES OF CHLOROBENZOIC AND BENZOIC ACIDS IN CESIUM CHLORIDE SOLUTIONS

CsCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0 25	1.030	0.01134	0.00950	0.071
.50	1.062	.01094	.00910	.074
1.00	1.124	.01015	.00851	.066
2.00	1.245	.00854	.00730	.066
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.2	1.024	0.0256	0.0252	0.108
.5	1.062	.0242	.0238	.093
1.0	1.124	.0223	.0220	.081

Here k for the sodium perchlorate lines is 0.065 in both Fig. 1 and Fig. 2. Larsson's value for benzoic acid at 18° is 0.050, while the results of Kolthoff and Bosch may be calculated to k values ranging from 0.051 to 0.080.

The slope of the cesium chloride line in Fig. 1 is 0.067. The two values given by Larsson for benzoic acid are "salting-in" constants indicating an increased solubility of molecular benzoic acid in solutions of cesium chloride. His calculations for k in 0.5 and 1.0 molar solutions are −0.008 and −0.009, respectively, at 18°. As this is the only case found in which there is a definite difference between the k values for *o*-chlorobenzoic acid and benzoic acid, solubility determinations were carried out with benzoic

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(12) Haeseler, Dissertation, Columbia University, 1929.

acid in cesium chloride solutions at 25°. These values are given in the second part of Table VII.

The "salting-out" constant is 0.092, slightly higher than the values for *o*-chlorobenzoic acid and not in agreement with the values of Larsson for benzoic acid. The explanation is offered that while the activity coefficients seem to be independent of temperature for the case of marked decrease in solubility, this is not the case where the "salting-in" effect is playing a more important role.

In Figs. 1 and 2 it is seen that for the chlorides the order of decreasing solubility is as expected from the ion sizes, the greater effect being due to the smaller ion, *i. e.*, Li>Na>K>Cs. For the anions, however, in accordance with the theory one would expect that if the cations "salt-out" the anions would "salt-in" and although in this case the predominant effect is still "salting-out," a comparison of potassium bromide with potassium chloride and sodium perchlorate with sodium chloride shows this effect. We shall now turn to salts which definitely "salt-in" the chlorobenzoic acids.

"Salting-In" of Chlorobenzoic Acids.—The "salting-in" effect of sodium *o*-chlorobenzoate on *o*-chlorobenzoic acid has already been cited in Table I. A similar effect in the case of benzoic acid with sodium benzoate has been interpreted by Kolthoff and Bosch to be attributable to the formation of anions of double molecules of benzoic acid. The chief reason for not accepting compound formation as a general explanation is that potassium benzoate "salts-in" benzene and nitrobenzene, while potassium chloride "salts-out" these substances.[13] A definite case of a general "salting-in" effect which must be attributed to the polar structure of the non-electrolyte is the "salting-in" of trinitrotriamminecobalt by potassium chloride.[14]

Table VIII gives the results for *o*- and *m*-chlorobenzoic acids and benzoic acid in sodium benzenesulfonate solutions.

The results indicate that equation (2) no longer holds. The *k* values are not the same as those found by Larsson. For benzoic acid in 0.01 molar buffer solutions containing 0.2, 0.5 and 1.0 mole of sodium benzenesulfonate, Larsson obtains *k* values of −0.134, −0.117 and −0.120 (at 18°).

Table IX gives the results of solubility determinations of benzoic and *o*-chlorobenzoic acids in sodium *p*-toluenesulfonate solutions.

From Tables VIII and IX it is seen that the activity coefficient is apparently dependent on the buffer ratio. Table X gives the results with sodium β-naphthalenesulfonate as the solvent salt. Due to the slight solubility of this salt the results could not be extended above 0.2 molar.

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[13] Private communication from P. M. Gross—from the Master's thesis of A. Whitenfish with J. H. Saylor and P. M. Gross.

[14] Brönsted, Delbanco and Volqvartz, *Z. physik. Chem.*, **162A**, 129 (1932).

TABLE VIII

SOLUBILITIES OF CHLOROBENZOIC AND BENZOIC ACIDS IN SODIUM BENZENESULFONATE SOLUTIONS

Sodium benzene-sulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid moles per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.011	0.01248	0.01045	−0.116
.5	1.032	.01381	.01164	− .140
.7	1.048	.01506	.01286	− .162
1.0	1.068	.01728	.01523	− .187
Solutions 0.05 molar in sodium salt. Correction = −0.00033				
0.5	1.033	0.01285	0.01199	−0.166
1.0	1.070	.01671	.01588	− .205
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.010	0.00226	0.00202	−0.122
.5	1.031	.00250	.00225	− .138
1.0	1.067	.00310	.00285	− .174
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.1	1.005	0.0274	0.0270	−0.079
.2	1.011	.0280	.0276	− .089
.5	1.033	.0308	.0304	− .120
1.0	1.068	.0393	.0389	− .167
Solutions 0.05 molar in sodium salt. Correction = −0.0005				
0.2	1.013	0.0284	0.0278	−0.100
.5	1.034	.0313	.0307	− .128
1.0	1.071	.0417	.0411	− .190

TABLE IX

SOLUBILITIES OF *o*-CHLOROBENZOIC AND BENZOIC ACIDS IN SODIUM *p*-TOLUENESULFONATE SOLUTIONS

Sodium *p*-toluene-sulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.011	0.01334	0.01130	−0.287
.5	1.032	.01668	.01447	− .329
.7	1.048	.01980	.01754	− .355
1.0	1.066	.02715	.02483	− .399
Solutions 0.05 molar in sodium salt. Correction = −0.00033				
0.2	1.015	0.01248	0.01166	−0.355
.3	1.022	.01364	.01276	− .367
.5	1.035	.01636	.01549	− .389
.7	1.048	.01964	.01877	− .397
1.0	1.069	.02721	.02630	− .425
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.2	1.014	0.0305	0.0301	−0.278
.5	1.035	.0378	.0373	− .298
1.0	1.066	.0620	.0616	− .366

Discussion

A general survey of the results with any of the acids indicates that for the same weak acid some salts "salt-out" while others "salt-in." In general, it would appear that for the carboxylic acids investigated, the anion of the solvent salt has very little if any "salting-out" effect, but rather that its general effect is to increase the solubility. This is interpreted to mean that the molecules of weak acid are oriented about the anion.

A comparison of the activity coefficients of the chlorobenzoic acids

TABLE X

SOLUBILITIES OF *o*-CHLOROBENZOIC AND BENZOIC ACIDS IN SODIUM β-NAPHTHALENESULFONATE SOLUTIONS

Sodium β-naphthalene sulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.10	1.005	0.01382	0.01176	−0.747
.15	1.008	.01513	.01285	− .757
.20	1.010	.01693	.01432	− .802
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.10	1.005	0.0313	0.0309	−0.670
.20	1.013	.0385	.0380	− .784

with benzoic acid is of particular interest in that the molecular solubility of the most soluble acid (benzoic) is approximately ninety-five times greater than the least soluble acid (*p*-chlorobenzoic) and the dissociation constant of the strongest acid (*o*-chlorobenzoic) is approximately twenty times greater than the weakest acid (benzoic). Table XI gives a summary of the "salting-out" constants for the different acids.

TABLE XI

THE "SALTING-OUT" CONSTANTS FOR BENZOIC AND ORTHO-, META- AND PARA-CHLOROBENZOIC ACIDS

Salt	Benzoic	*o*-Chlorobenzoic	*m*-Chlorobenzoic	*p*-Chloro benzoic
$NaClO_4$	0.060[a]	0.065	0.065	..
CsCl	.092[b]	.067	..	..
KBr	.108[c]	.099	.090	..
KCl	.138[d]	.139	.142	0.138
NaCl	.177[e]	.182	.180	..
LiCl	.192[f]	.193	.193	.

[a] Average value from Kolthoff and Bosch.

[b] Larsson gives −0.009 and −0.008 at 18°. See Table VII.

[c] Calculated from Haeseler's results (corrected).

[d] From the results of Chase and Kilpatrick.

[e,f] From Larsson.

From the table it is seen that in cases of "salting-out" the constant is practically the same for all four acids, that is, the activity coefficients of each acid are the same at the same concentration of a given salt. This is illustrated graphically for the case of potassium chloride as solvent salt in Fig. 3. Evidently this is a case in which a highly polar carboxyl group plays the predominating role in the "salting-in" process and the substitution of a chlorine atom in the phenyl group is without effect on the activity coefficient.

Summary

From determinations of the total solubility of the monochlorobenzoic acids in aqueous salt solutions the molecular solubilities and the activity coefficients have been obtained.

For the same weak acid some salts "salt-out" and others "salt-in." An explanation has been offered based on the work of Kruyt and Robinson.

The activity coefficients of the molecules of the monochlorobenzoic and benzoic acids are the same at corresponding concentrations of the same salt.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The "Salting-out" and "Salting-in" of Weak Acids. II. The Activity Coefficients of the Molecules of Ortho, Meta and Para-Hydroxybenzoic Acids in Aqueous Salt Solutions[1]

BY ARTHUR OSOL AND MARTIN KILPATRICK

In the preceding paper it was shown that for the monochlorobenzoic acids the activity coefficients of the molecular part of these acids were the same at corresponding concentrations of the same salt. The present paper deals with the activity coefficients of ortho, meta and para-hydroxybenzoic acids.

Experimental Part

The experimental method was essentially the same as that given in the preceding paper. The acids were purified by recrystallization and melted at 159, 201 and 214° for the ortho, meta and para acids, respectively. The total solubilities were 0.01598, 0.0706 and 0.0451 mole per liter, from which the molecular solubilities at zero ion concentration, calculated from the K_a and K_c/K_a ratios as before, were found to be 0.01217, 0.0683 and 0.0440 mole per liter for the ortho, meta and para-hydroxy acids, respectively. The corrections for the buffer salts are given in each table. Table I gives the results in potassium chloride solutions.

From Table I it is evident that the activity coefficients are not the same for the three acids as in the case of the monochloro substituted acids. The "salting-out" constants decrease in the order ortho ($k = 0.122$), meta ($k = 0.115$), para ($k = 0.095$) as compared with benzoic acid ($k = 0.138$). Table II gives the results with sodium chloride.

The slope of the line for *o*-hydroxybenzoic acid in sodium chloride solutions in Fig. 1 is 0.172 as compared with 0.177 for benzoic acid.

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[1] Abstracted from the dissertation of Arthur Osol presented April 1, 1933, to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Paper presented in part before the Washington meeting of the American Chemical Society, March, 1933.

TABLE I

SOLUBILITIES OF HYDROXYBENZOIC ACIDS IN POTASSIUM CHLORIDE SOLUTIONS

o-Hydroxybenzoic Acid

Solutions 0.01 molar in sodium salt. Correction = −0.00031

KCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
0.2	1.008	0.01353	0.01144	0.132
.5	1.021	.01252	.01049	.129
1.0	1.042	.01096	.00919	.122
1.5	1.064	.00945	.00796	.123
2.0	1.087	.00833	.00704	.119

m-Hydroxybenzoic Acid

Solutions 0.01 molar in sodium salt. Correction = −0.0002

KCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
0.2	1.010	0.0657	0.0648	0.114
.5	1.024	.0606	.0596	.118
1.0	1.044	.0529	.0521	.118
1.5	1.067	.0470	.0463	.113
2.0	1.088	.0399	.0393	.119

p-Hydroxybenzoic Acid

Solutions 0.01 molar in sodium salt. Correction = −0.0002

KCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
0.2	1.009	0.0430	0.0426	0.071
.5	1.023	.0399	.0395	.091
.7	1.030	.0381	.0377	.096
1.0	1.043	.0354	.0350	.099
1.5	1.066	.0323	.0320	.092
2.0	1.088	.0289	.0286	.094
2.5	1.109	.0256	.0253	.096

TABLE II

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN SODIUM CHLORIDE SOLUTIONS

Solutions 0.01 molar in sodium salt. Correction = −0.00031

NaCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
0.2	1.005	0.01326	0.01120	0.179
.5	1.018	.01188	.00993	.176
1.0	1.039	.00984	.00821	.171
2.0	1.076	.00666	.00556	.170

TABLE III

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN LITHIUM CHLORIDE SOLUTIONS

Solutions 0.01 molar in sodium salt. Correction = −0.00031

LiCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
0.5	1.010	0.01194	0.00979	0.189
.673	1.014	.01104	.00901	.194
1.198	1.025	.00882	.00713	.194
2.067	1.047	.00607	.00493	.190

TABLE IV

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN POTASSIUM BROMIDE SOLUTIONS

Solutions 0.01 molar in sodium salt. Correction = −0.00031

KBr moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
0.2	1.014	0.01381	0.01168	0.089
.5	1.038	.01308	.01099	.088
1.0	1.080	.01185	.00998	.086

TABLE V

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN SODIUM PERCHLORATE SOLUTIONS

Solutions 0.01 molar in sodium salt. Correction = −0.00031

$NaClO_4$ moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
0.472	1.034	0.01400	0.01190	0.021
.500	1.038	.01396	.01186	.022
1.000	1.076	.01338	.01155	.023
1.103	1.082	.01332	.01153	.021
1.863	1.141	.01215	.01075	.029

It is to be observed that for those salts producing the greatest decrease in solubility the differences in the values of *k* for benzoic and *o*-hydroxybenzoic acids are small. As shown in Table III the difference in the case of lithium chloride has disappeared. This is interpreted to mean that the effect of the introduction of the hydroxy group is to increase the "salting-in" by the anion, the effect being detectable for the larger cations which have smaller "salting-out" effects.

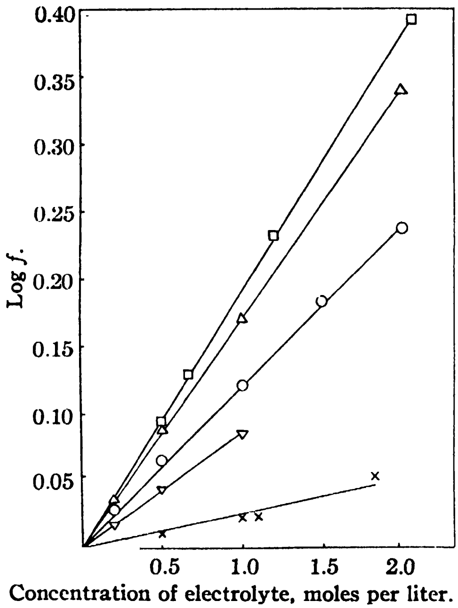

Fig. 1.—Activity coefficients of molecular *o*-hydroxybenzoic acid in salt solutions: ×, $NaClO_4$; ▽, KBr; △, NaCl; □, LiCl; ○, KCl.

In Tables IV and V the differences in the "salting-out" constants are still greater. Figure 1 presents graphically the results for salicylic acid. If our picture is correct, one would expect even greater "salting-in" constants (smaller activity coefficients) for the hydroxybenzoic acids in sulfonate solutions. Table VI shows this to be the case.

Table VII gives a comparison of the "salting-out" constants for the various salts which follow the law: $\log f = kC$.

TABLE VI

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN SULFONATE SOLUTIONS

Conc. sulfonate moles per liter	Density g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt				
Correction = −0.00031				
In Sodium Benzenesulfonate				
0.10	1.005	0.01447	0.01234	−0.060
.25	1.015	.01545	.01307	− .124
.50	1.033	.01728	.01475	− .167
1.00	1.070	.02349	.02082	− .233
In Sodium *p*-Toluenesulfonate				
0.20	1.014	0.01677	0.01437	−0.361
.50	1.032	.02191	.01922	− .397
1.00	1.066	.03903	.03708	− .484
In Sodium β-Naphthalenesulfonate				
0.1	1.005	0.01790	0.01543	−1.03
.2	1.010	.02295	.01983	−1.06

The results for potassium chloride are given in Fig. 2. As shown in Fig. 3 of the preceding paper the results for the monochlorobenzoic acids coincide with those of benzoic acid. Evidently the introduction of the hydroxy group diminishes the decrease in solubility and increases the "salt-

TABLE VII

THE "SALTING-OUT" CONSTANTS FOR BENZOIC AND ORTHO-, META- AND PARA-HYDROXYBENZOIC ACIDS

Salt	Benzoic	o-Hydroxybenzoic	m-Hydroxybenzoic	p-Hydroxybenzoic
$NaClO_4$	0.060	0.026		
KBr	.108	.087		
KCl	.138	.122	0.115	0.095
NaCl	.177	.172		
LiCl	.192	.191		

ing-in" effect. The point of view that the molecules of the acid are more readily oriented on the anion upon the introduction of the polar hydroxy group seems to be in accord with the experimental results. In the case of other substituted benzoic acids it would appear that the effect of the introduction of a nitro group[2] would be similar to that of the chloride, while an amino group would have an effect like that of the hydroxy group.[3]

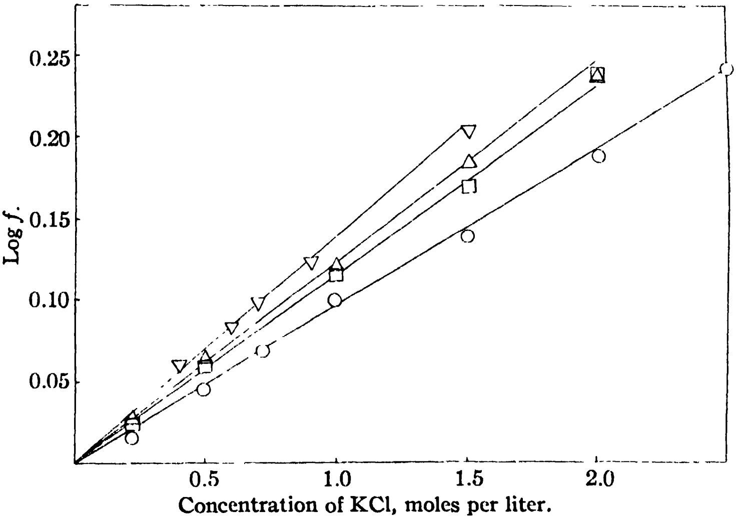

Fig. 2.—Activity coefficients of molecular benzoic, ortho, meta and para-hydroxybenzoic acids in KCl solutions: △, ortho, ○, para; □, meta; ▽, benzoic.

In concluding it should be pointed out that there should be cases in which the cation has a "salting-in" effect and the anion a "salting-out" effect, but in general the "salting-out" effect of the anions will probably be less than that of cations. One such case has been cited by Kruyt and Robinson from the data of Linderstrøm-Lang.[4]

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(2) Randall and Failey, *Chem. Rev.*, **4**, 291 (1927).

(3) Rørdam, Dissertation, Copenhagen, 1925.

(4) Kruyt and Robinson, *Proc. Acad. Amsterdam*, **29**, 1244 (1926); Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, No. 4 (1924).

Summary

The activity coefficients of molecular salicylic acid have been determined in various aqueous salt solutions.

For the hydroxybenzoic acids the "salting-out" constants diverge from the values for benzoic acid as one progresses from salts having the highest "salting-out" effects to salts having the lowest effects.

A comparison of the "salting-out" constants for ortho, meta and parahydroxybenzoic acids in potassium chloride solutions shows that the constants decrease with the transfer of the hydroxy group to the meta and para positions, respectively.

PHILADELPHIA, PENNSYLVANIA

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XVI. A Further Study of the Chlorination of Benzene

BY HOMER P. SMITH, W. ALBERT NOYES, JR., AND EDWIN J. HART

In a previous article[1] a report was made of an investigation of certain phases of the chlorination of benzene vapor. The results may be briefly summarized as follows. (1) The rate of reaction was at least approximately proportional to the pressure of the chlorine. Benzene and chlorine pressures of comparable magnitude (several centimeters) were used. (2) A liquid was formed first on the walls, followed by the gradual growth of crystals. The liquid was not analyzed. It may have been either phenyl chloride or a solution of benzene in some of the reaction products. (3) The only product isolated and for which a definite analysis was obtained was benzene hexachloride ($C_6H_6Cl_6$). (4) From measurements of pressure change and determination of the chlorine used up it was obvious that both addition and substitution were taking place.

In the present investigation an attempt has been made to elucidate certain aspects of benzene chlorination through measurements of quantum yields, pressure changes and reaction rates. In so far as the experimental results may be compared with those previously reported, complete agreement is noted. It was hoped to simplify the results by using benzene pressures so low that the first substitution product (phenyl chloride) would not condense.

I. Experimental Procedure

(a) **Chlorine.**—In some of the experiments the chlorine was prepared by heating anhydrous cupric chloride. Water was first removed from hydrated cupric chloride by heating for several days at 135° under a high vacuum. The chlorine was evolved at temperatures of several hundred degrees, was dried by phosphorus pentoxide and fractionally distilled repeatedly. It was kept at the temperature of solidification of ammonia (−77°) and was admitted to the reaction system as desired.

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[1] Lane and Noyes, THIS JOURNAL, 54, 161 (1932).

In most of the experiments carefully purified commercial chlorine was used. A diagram of the purification system is shown in Fig. 1. The chlorine cylinder was attached at A, and G was connected to a water pump through drying columns. The system between G and A was evacuated with the water pump and chlorine admitted from the cylinder at first intermittently and then in a steady stream. The trap C was surrounded with solid–liquid ammonia mush and an appreciable amount of chlorine condensed. The vapor pressure of chlorine at this temperature is about 6 cm., so that danger of back diffusion of water vapor was very small. The drying tube E was filled with magnesium perchlorate. When sufficient chlorine had collected in C, the tube at A was sealed off. After further removal of some of the chlorine, the tube at G was sealed off and most of the chlorine was distilled into the trap F, the final portion being left in C by sealing the tube at B. The chlorine was distilled back and forth between F and D in order to dry it.

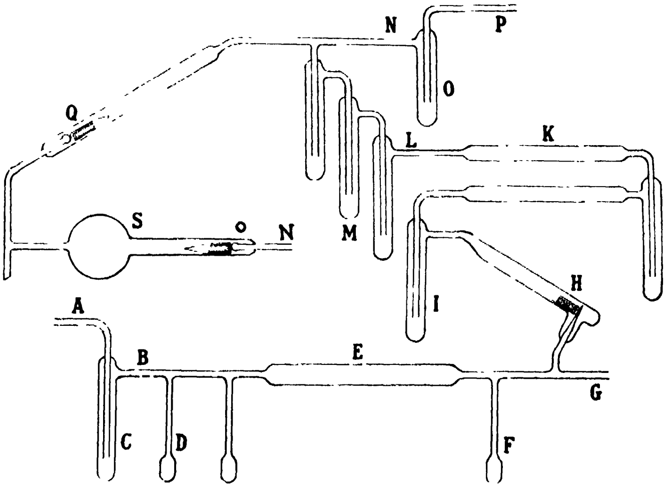

Fig. 1.

The rest of the line as far as H had been thoroughly evacuated with continual flaming, liquid air being kept around the trap at O to remove mercury vapor and other impurities. By means of the glass-surrounded iron bar in H the tip was broken while the chlorine in F was kept cold by liquid air. The entire system was next evacuated to remove traces of non-condensable gases and then the chlorine was distilled into the trap I. There followed repeated distillation through the drying tubes K filled with magnesium perchlorate, succeeded by a fractional distillation in which most of the chlorine was finally sealed off in the main line at L. The chlorine was now distilled through the three traps M, a high vacuum being maintained during each distillation to eliminate the last traces of uncondensable gases. Finally the line was sealed off at N.

The flasks in which the chlorine was finally collected are shown at S. They had been maintained at a high vacuum in a furnace heated to a high temperature (about 400–450°) for several days, the mercury vapor and other condensable impurities being removed by a trap immersed in liquid air. When the purified chlorine was collected in the final trap M, the tip in Q was broken and the chlorine admitted to the flasks S at any desired pressure. The flasks were sealed off and kept for use. In some cases the chlorine reservoir was attached to a series of breakable tips such as that shown at Q so that it could be used repeatedly to admit chlorine to reaction vessels without allowing contact with the air.

(b) **Benzene.**—The benzene used in these experiments had been specially purified by Dr. R. A. Vingee[2] for use in freezing point determinations. It showed no test for thiophene and gave a constant and reproducible melting point of 5.452 ± 0.003°. It was kept over phosphorus pentoxide and after outgassing was never allowed to come into contact with the air.

(c) **Pressure Measurements.**—Pressures in systems where chlorine was present were measured by Pyrex gages of the Bodenstein type used as null instruments. The sensitivities of the gages varied from about 1 millimeter to about 0.02 millimeter. The outside pressures were usually read with sulfuric acid manometers. Temperature corrections were always applied.

(d) **Quantum Efficiency Determinations.**—The absorption coefficients of chlorine have been determined by von Halban and Siedentopf.[3] The values given by these authors were used in the calculations. Several determinations of the absorption coefficient were made using the 4358 Å. line of mercury. The average value agreed with that of von Halban and Siedentopf for this wave length to better than one per cent.

One source of error in these determinations is due to the formation of a solid product on the window of the reaction vessel, particularly at the point where it is traversed by a beam of radiation. In early runs no attempt was made to eliminate this error and values for the quantum yield were found to show little consistency.

A large variety of different chlorinated products may be formed during the course of the reaction. For this reason the apparent quantum efficiency probably will change with the ratio of molecules of chlorine disappearing to molecules of benzene initially present. It was decided, therefore, to attempt to determine the quantum efficiency only for the early stages of the reaction. Under these conditions the accuracy of the quantum yield will be determined largely by the error in the difference between the initial and final chlorine pressures. Since the difference is small compared to either quantity alone the precision will leave something to be desired.

The preparation of the reaction vessels may be best described by reference to Fig. 1. A chlorine bulb of the type S was sealed through the tube N to a Pyrex flask which in turn was sealed to a vacuum line. The flask was evacuated with continual flaming for several hours and benzene vapor admitted to the desired pressure. The vessel was then sealed off. In some cases the benzene vapor was condensed in the reaction vessel with liquid air in order to avoid any thermal decomposition upon sealing. The tip o was broken and the chlorine admitted to the reaction vessel. After waiting a few seconds for pressure equilibrium to be attained but before benzene could diffuse into S, the tube N was sealed off. The reaction vessel then contained a mixture of chlorine and benzene whose total pressure equaled the pressure of the chlorine remaining in S. After exposure of the reaction vessel to radiation the tip was broken under a potassium iodide solution and the flask filled. After emptying and rinsing the liberated iodine was titrated with approximately $N/20$ sodium thiosulfate. In the same manner the chlorine in the bulb S was determined. The volumes of all parts of the apparatus were accurately determined by filling with water from calibrated burets. The calculation of the amount of chlorine disappearing was accomplished as follows. If p_1 is the initial pressure of the benzene in the reaction vessel up to the breakable tip in o and V_1 is the volume of the reaction vessel, then if V_2 is the volume of the reaction vessel after being sealed off, the pressure of the benzene in the reaction vessel as exposed to radiation is

$$p_3 = V_1p_1/V_2 \tag{1}$$

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[2] R. A. Vingee, Thesis, Brown University, 1931.

[3] Von Halban and Siedentopf, *Z. physik. Chem.*, **103**, 71 (1922).

The pressure of the chlorine (p_4) in the bulb S may be determined from the volume and the analysis. The initial pressure of chlorine in the reaction vessel before exposure to radiation is, therefore

$$p_5 = p_4 - p_3 \tag{2}$$

The final pressure of chlorine in the reaction vessel after exposure (p_6) is obtained from the volume and the titration. All of the information for calculating the number of moles of chlorine which have disappeared during exposure to radiation is now available.

In any chain reaction involving chlorine the effects of impurities are difficult to estimate and account for. In our opinion most of the error is to be ascribed to the quantity ($p_6 - p_5$) which is always small compared to either p_6 or p_5.

Careful test showed that for times of exposure similar to those indicated in Table I the thermal reaction may usually be ignored.

The thermopile was of the Moll micro type with small surface. It was calibrated at frequent intervals with two radiation standards furnished by the Bureau of Standards. The value obtained was 4.76 ergs/sq. mm./sec./cm. deflection.

Due to the fact that the reaction vessel had a curved surface it was necessary to use a beam of radiation of small cross section. The transmission of the walls did not seem to vary greatly with the wave length (4358 and 3660 Å.) and the thickness of the glass. The average of several determinations gave 0.85 as the fraction of the radiation transmitted. At 3130 Å. corex flasks were used and these showed a wall transmission of 0.84 for this wave length.[4]

A shield of asbestos board perforated by a hole 6.355 mm. in diameter was placed in the path of an approximately parallel beam of radiation. In most of the runs a quartz monochromator was used, although an attempt was made to use color filters at 4358 Å. in order to secure greater intensity. Capillary quartz mercury arc lamps somewhat similar to those described by Forbes and Harrison[5] were used. The thermopile, whose surface was slightly larger than that of the opening in the shield, was used to measure the total radiation penetrating the opening. The deflection obtained with the shield in position was 0.818 times the deflection obtained with the shield removed, whereas the ratio of the area of the spot to the area of the thermopile window was 0.846. The ratio was determined for several different types of beam and was surprisingly constant as long as the area of the beam was slightly larger than that of the thermopile window. Some error would undoubtedly be introduced by a non-homogeneous beam or by a highly diverging or converging beam, but such errors are small in this case compared to errors due to other causes. In the calculations, therefore, the observed deflection is divided by 0.818 and the area of the perforation is taken as the area to be used in the calculation.

The intensity of the radiation penetrating the perforation was determined at frequent intervals and the flask exposed for measured time intervals. The product of the galvanometer deflection and the time was determined and used. The fraction of the radiation absorbed by the chlorine was calculated from the pressure, the diameter of the flask and the absorption coefficients of von Halban and Siedentopf.[3] For 3660 Å. and 3130 Å. the reflection from the back wall of the flask could be neglected.

During the run the flask was turned at frequent intervals to avoid areas covered by solid deposit.

(e) **Pressure Change during Reaction.**—In order to follow the course of the reaction a system of the type shown in Fig. 2 was used. The entire apparatus was built of Pyrex. The mercury arc lamp in the center was surrounded by a water jacket which in turn was surrounded by a tube containing a solution of iodine and bromine dissolved in carbon tetrachloride. The radiation was, therefore, not strictly monochromatic, although the 3660 Å. line was the most intense by far. This apparatus had, however, the advantage of giving reproducible results with sufficient energy absorption to permit carrying the reaction to near completion in a finite length of time. Crude estimates of the quantum efficiency agreed as to order of magnitude with those obtained by the other method. The total pressure in the system was followed with a Bodenstein manometer.

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[4] The authors wish to express their appreciation to the Corning Glass Co. for furnishing the corex bulbs and tubing.

[5] Forbes and Harrison, THIS JOURNAL, 47, 2449 (1925).

In some instances attempts were made to determine the chlorine pressure by optical absorption in an auxiliary cell. For various reasons, mainly due to a slight deposition of solid on the windows of the auxiliary cell, great accuracy was not attained by this method. At the end of the run chlorine was determined as described above. After the end-point had been reached with thiosulfate, the hydrogen chloride was titrated using approximately $N/100$ sodium hydroxide with methyl orange as the indicator. In this way it was possible to determine the relative amounts of addition and substitution.

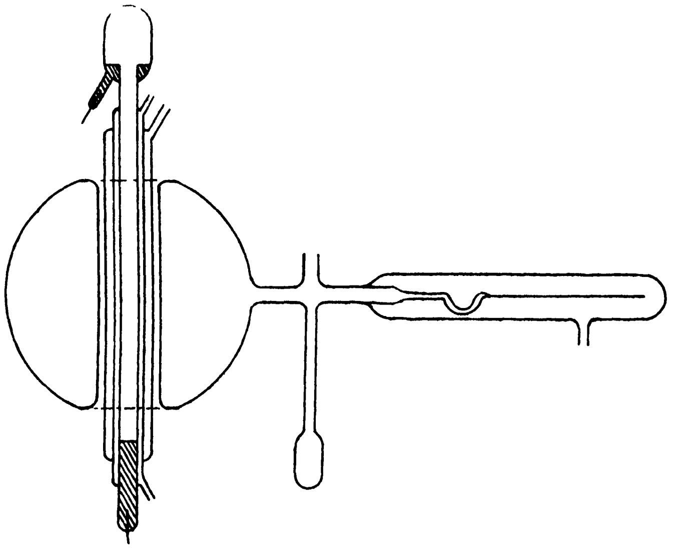

Fig. 2.

II. Results

Preliminary investigations by several different methods served to show definitely that the reaction is of the chain type and that the quantum yield tends to increase with the ratio $(P_a - P_x)/P_m$ (P_a = initial chlorine pressure, P_x = chlorine pressure at time t, P_m = initial benzene pressure). It seems probable that the recombination of chlorine atoms is effective in stopping the chains so that the geometry of the beam of radiation would affect the apparent yield. For these reasons Table I includes only results obtained by the method described in the preceding section for which the above ratio is between 0.15 and 0.50. Disagreement between found and calculated values may be accounted for, with one exception, by variations in the distribution of the absorbed intensity. Correction for dark reaction has been made where necessary.

TABLE I

QUANTUM EFFICIENCY OF BENZENE CHLORINATION, 25 ± 2°

Wave length	Galv. defl., av.	Percentage absorbed	Initial pressure of Cl_2, mm.	Initial pressure of C_6H_6, mm.	Pressure change of Cl_2, mm.	Quantum efficiency Found	Quantum efficiency Calcd.
3660	4.8	84	94.7	8.56	1.54	22	(22)
	18.6	91	125.2	8.40	2.52	12	14
	...	..	113.1	8.00	0.07	..	..
	2.4	90	119.3	8.51	1.91	23[a]	..
	8 5	89	116.1	8.30	4.64	25[b]	..
	35.5	83	97.1	40.8	10.23	46	40
	17.3	90	122.2	40.9	5.81	34	69
3130	8.8	99	121.3	9.65	3.00	16	22
	5.5	99	126.4	8.40	2.50	17	25
	...	..	150.5	9.3	+0.44[c]	..	..
	...	..	178.6	8.1	2.00[d]	..	..

[a] Pressure of added oxygen, 0.162 mm. [b] Pressure of added oxygen, 0.153 mm. [c] Blank run 74 min. at 97°. [d] Blank run twenty hours at room temp.

In all of the runs shown in Table I titrations for hydrogen chloride were made. As will be shown later the initial reaction is almost entirely one of addition, so that with a small ratio of molecules of chlorine used to benzene pressure little hydrogen chloride should be found. The amount did not

TABLE II

PRESSURE CHANGES DURING BENZENE CHLORINATION

Run	Time, hrs.	Initial pressure of Cl_2, mm.	Initial pressure of C_6H_6, mm.	Final total pressure, mm.	Final pressure of Cl_2, mm.	Final pressure of HCl, mm.	Temp., °C.
1[a]	58	44.3	9.2	22.45	10.95	..	24
2	14.25	35.64	1.80	30.29	...	10.0	24.5
3	1.75	40.01	12.5	22.43	4.79	12.20	26
4	0.33	139.0	9.54	113.72	85.37	27.52	27
5[b]	20.5	61.30	4.61	49.70	33.96	15.80	24.7
6	1.13	40.06	2.32	34.18	27.27	7.54	24.7
7	1.15	39.27	2.49	35.36	28.43	6.08	34.6
8	1.55	40.65[c]	1.63	37.75	30.73	6.79	34.2
9	15.00	71.98	3.25	63.91	49.69	12.51	25.1
10	0.17	55.42	1.66	54.23	51.29	0.57	25.0
11	.24	40.74	1.95	40.92	37.90	.85	35.2
12	.24	40.07	2.18	38.43	35.17	1.90	25.1
13[d]	.88	38.64	1.54	34.62	28.93	5.54	24.8
14	1.02	39.16	2.32	38.71	35.15	2.07	34.7
15	0.565	38.18	2.13	37.96	34.55	1.70	34.8
16[e]	.667	40.47	2.22	...	32.24	4.03	35.0
17[e]	.50	40.28	3.03	...	27.92	4.45	25.0

[a] Run No. 1 was made with a dichromate filter. All others were made with approximately monochromatic 3660 Å. radiation. [b] A thermostat was used beginning with Run No. 5. [c] A small amount of air was probably present in Run No. 8. [d] Beginning with Run No. 13 a new reaction vessel was used. [e] No pressure gage was used during Runs 16 and 17.

exceed the experimental error in those runs shown. The dark reaction, however, seemed to be mainly one of substitution, for the chlorine pressure change usually agreed approximately with the pressure of the hydrogen chloride found.

Table II presents data obtained with the apparatus shown in Fig. 2.

From the data in Table II it is possible to calculate empirical formulas for the products by assuming that the benzene is completely used up. Since most of the runs did not approach complete chlorination, the empirical formulas will not be in accord. Table III gives the empirical formulas together with the ratio of molecules of chlorine added to molecules substituted.

TABLE III

EMPIRICAL FORMULAS OF PRODUCTS, $C_dH_eCl_f$ ($d = 6$)

Run	e	f	$e + f$	Molecules added/ molecules subs.	Temp., °C.
2	0.4	11.5	11.9	0.53	24.5
3	5.0	4.7	9.7	1.9	26
4	3.1	8.4	9.5	0.95	27
5	2.6	8.4	11.0	.73	24.7
6	2.8	7.8	10.6	.70	24.7
7	4.1	5.7	9.8	.78	34.6
8	1.8	8.0	9.8	.46	34.2
9	2.2	9.9	12.1	.78	25.1
10	5.7	4.6	10.3	6.25	25.0
11	5.6	2.5	8.1	2.34	35.2
12	5.1	2.6	7.7	1.58	25.1
13	2.4	9.0	11.4	0.75	24.8
14	5.1	2.6	7.7	.94	34.7
15	5.2	2.6	7.8	1.14	34.8
16	4.2	5.6	9.8	0.96	35.0
17	4.5	6.7	11.2	1.78	25.0

It is evident that both addition and substitution take place to a large extent in the chlorination of benzene. At 25° the ratio of molecules added to molecules substituted approaches 0.5 as a lower limit and the number of molecules reacting per benzene molecule approaches 9. This indicates definitely that the chlorination may, if carried on for a sufficient length of time, go as far as dodecachlorocyclohexane (C_6Cl_{12}). The only sharp melting point for products was obtained after run 2. This product melted at 66–68° which may be taken tentatively as the melting point of C_6Cl_{12}.

At 25° it is found empirically that

$$\text{Moles substituted/moles added} = 2/9(P_a - P_x)/P_m \qquad (3)$$

Since the vapor pressure of benzene hexachloride is negligible we may write, if there are no intermediate addition products

$$\text{Chlorine added} = 3/4(P_0 - P) \qquad (4)$$

where P_0 is the initial total pressure and P is the total pressure at the time t.

Hence

$$(P_0 - P) = 12\,P_m(P_a - P_x)/(9P_m + 2(P_a - P_x)) \qquad (5)$$

At 35° it is found empirically that

$$(P_0 - P) = 12.552\,P_m(P_a - P_x)/(9P_m + 2(P_a - P_x)) - 1.27 \qquad (6)$$

Figure 3 shows the applicability of equations (5) and (6). These equations may be used with some certainty to calculate the chlorine pressure after early stages of a run.

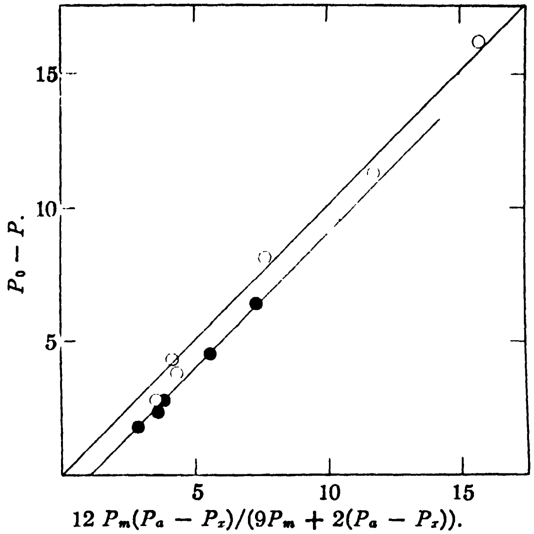

Fig. 3.—Upper line —25° Lower line —35°

At 25°

$$P_H = 2(P_a - P_x)^2/(9P_m + 2(P_a - P_x)) \qquad (7)$$

and

$$-dP_H/dP_x = 0,\ P_a = P_x \qquad (8)$$

where P_H is the pressure of the hydrogen chloride formed. The addition reaction is, therefore, predominant at the beginning of a run at this temperature. At 35° the analogous expression for hydrogen chloride pressure agrees well within experimental error with the observations.

Several rate expressions were tried, especially the following. *I. Rate* proportional to absorbed intensity[6]

$$aI_0t = P_a - P_x + (1/k)\log_{10}(e^{-kP_a} - 1)/(e^{-kP_x} - 1) \qquad (9)$$

where $k = 2.303\,Kd$, d is the thickness of the cell (3.5 cm. av.) and K is the absorption coefficient in the expression $I = I_0\,10^{-KdP_x}$, I_0 = incident intensity, I = intensity transmitted.

II. Rate proportional to square root of absorbed intensity

$$aktI_0^{1/2} = 4.606\log_{10}(e^{kP_a/2} + \sqrt{e^{kP_a} - 1})/(e^{kP_x/2} + \sqrt{e^{kP_x} - 1}) \qquad (10)$$

III. Rate proportional to chlorine pressure

$$2.303\log_{10} P_a/P_x = k_1t \qquad (11)$$

IV. Rate proportional to square of chlorine pressure

$$(1/P_x - 1/P_a) = k_2t \qquad (12)$$

Table IV illustrates the application of equations 9, 10, 11 and 12 to three different runs. Constants are calculated for alternate pressure readings.

A slight deposition of solid product always occurs so that a slight decrease in light intensity during a run is to be expected. In no case is k_2 satisfactory, whereas in agreement with previous work,[1] k_1 holds approxi-

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(6) Romeyn and Noyes, THIS JOURNAL, 54, 4149 (1932).

TABLE IV

DEPENDENCE OF RATE ON CHLORINE PRESSURE

Time, min.	P, mm.	$k_1 \times 10^3$ Eq. 11 1/min.	$k_2 \times 10^4$ Eq. 12 1/min./mm. P	aI_0 Eq. 9	$aI_0^{1/2}$ Eq. 10
Run No. 3 (26°)					
0	52.51				
3.5	45.95	39	11.3	4.1	2.4
7.0	41.57	36	12.6	3.6	1.9
14.5	35.42	36	16.8	3.5	1.7
25.5	29.83	34	20.6	3.1	1.3
35.0	27.45				
Run No. 13 (24.8°)					
0	40.18				
2.0	39.57	7.7	2.0	0.81	0.49
3.5	39.00	10.0	2.7	1.05	.63
5.0	38.42	11.9	3.2	1.24	.74
6.4	37.88	12.4	3.5	1.29	.77
9.8	36.92	13.8	4.0	1.43	.83
12.0	36.31	15.7	4.7	1.61	.91
14.5	35.80	15.8	4.9	1.61	.90
17.8	35.25	15.9	5.2	1.61	.89
21.3	34.82				
Run No. 15 (34.8°)					
0	40.31				
3.8	40.25	4.2	1.11	0.45	0.26
8.8	39.90	1.9	0.51	.20	.14
11.5	39.68	2.2	.62	.24	.14
13.5	39.51	2.1	.59	.23	.12
19.0	39.11	2.1	.58	.22	.13
24.0	38.77	2.5	.70	.26	.16
29.0	38.35	2.5	.70	.26	.15
33.9	38.07				

mately for high benzene pressures. The choice between aI_0 and $aI_0^{1/2}$ is not clear-cut, although the latter shows the smallest average deviation from the mean. For other reasons the square root equation is probably to be preferred.

When one compares different runs it becomes obvious that the values of none of the constants are independent of either the initial chlorine or the initial benzene pressure. During the course of a given run it is difficult to introduce a quantity dependent on the unchlorinated benzene, but attempts showed that such terms were relatively unimportant. It seems difficult if not impossible to arrive at a formulation of the reaction rate for a complete run in terms of an equation which would have an unambiguous theoretical significance. A comparison of the rates of change of total pressure at the beginning of the various runs indicated that a relatively simple equation would hold. This equation may be written

$$-\mathrm{d}P/\mathrm{d}t = aI_0^{1/2}(1 - e^{-kP_a})^{1/2}P_aP_m \tag{13}$$

Integration of equation (13) is impossible without expressing the benzene pressure as a function of the chlorine pressure. This would involve the introduction of doubtful assumptions. It is possible to use equation (13) only to evaluate the initial slope of the total pressure–time curve.

In Table II five runs, Nos. 5, 6, 9, 10 and 12, were carried out in the same reaction vessel under comparable conditions. Of these No. 5 showed a very slow initial rate of change of total pressure. This phenomenon was occasionally encountered and has not been completely elucidated. Table V shows the applicability of equation (13) to the other four runs. The initial slopes were obtained graphically from large-scale plots of total pressure against time.

TABLE V

INITIAL RATE OF CHANGE OF TOTAL PRESSURE AT 25°

Run	6	9	10	12
$-\mathrm{d}P/\mathrm{d}t$, $t = 0$, mm./min.	0.208	0.775	0.282	0.260
$(1 - e^{-kP_a})^{-1/2}$	1.631	1.323	1.445	1.631
$-(P_aP_m)^{-1}(1 - e^{-kP_a})^{-1/2}\mathrm{d}P/\mathrm{d}t$	3.7×10^{-3}	4.4	4.4	4.9

Similar calculations for Runs 7, 8, 11 at 35° gave 1.7, 1.7 and 2.5 × 10^{-3} for the quantity in row 4.

The agreement in the fourth row of Table V is probably as good as one could expect. Reference to the quantum efficiencies in Table I shows that with one exception they may be fairly well accounted for by equation (13). The calculated quantum efficiencies are relative values based on the first. For reasons already discussed there should be some difference between the values at 3660 Å. and those at 3130 Å. When the rate of a reaction is proportional to the square root of the light intensity, the quantum efficiency will be inversely proportional to that quantity.

A comparison of the runs at 35° with those at 25° indicates in every case that less chlorine disappears in unit time at the higher temperature. Since the pressure gage was always at room temperature, it was suspected that some of the products might have condensed in the cooler parts of the system thus removing them from the zone in which chlorine atoms were produced. Two runs (Nos. 16 and 17) were made in which no pressure gage was used and in which all parts of the reaction system were at the temperature of the thermostat.

There are several runs at the two temperatures which may be compared more or less directly. For this purpose a constant was calculated from the initial and final chlorine pressures by the equation

$$2(P_a^{1/2} - P_x^{1/2}) = k_{1/2}\, t \tag{14}$$

Since the pressure of the chlorine is relatively low and the light absorption not large, this constant ($k_{1/2}$) should be very approximately proportional to $a\,I_0^{1/2}$ in equation (10). Table VI shows values of $k_{1/2}$ for pairs of comparable runs at 35° and at 25° together with $k_{1/2}/P_aP_m$ which should be roughly comparable to the values in the fourth row of Table V.

TABLE VI

EFFECT OF TEMPERATURE ON REACTION RATE

Run	$k_{1/2}$	$R = k_{1/2}/P_aP_m$	R_{35}/R_{25}
6	0.0338	3.64×10^{-4}	0.76
7	.0271	2.77×10^{-4}	
12	.0547	6.26×10^{-4}	.62
11	.0310	3.90×10^{-4}	
13	.0339	5.70×10^{-4}	.67
16	.0342	3.81×10^{-4}	
17	.0742	6.08×10^{-4}	.63

Since Runs 6 and 7 were for longer time intervals than the others shown in Table VI, R_{35}/R_{25} for this pair should be nearer unity than for the others.

It is evident that the net rate of chlorine disappearance is lower at 35° than it is at 25° under comparable conditions. The current through the mercury arc and the potential drop were maintained as nearly the same for the various runs as possible, but there remained the possibility of a variation in intensity either due to the arc itself or to the transmission of the color filter. In order to test this point the uranyl sulfate–oxalic acid actinometer was employed. This system has been studied with great care by Leighton and Forbes.[7] Due to the type of cell employed in these runs all of the precautions observed by these authors could not be followed. In particular the solution could not be stirred. Although too great accuracy should not be claimed for the variation of light intensity with temperature, the evidence indicated little or no change between 25 and 35°. It seems necessary to conclude, therefore, that not only the rate of disappearance of chlorine is lower at the higher temperature but that the quantum efficiency and the rate of change of total pressure are both lower. Possible explanations of this fact will be brought out in the discussion.

III. Discussion of Results

In the previous section empirical equations correlating most of the results on the chlorination of benzene have been given. It remains to give some theoretical justification for these equations and, if possible, to indicate the relationship between these results and the accepted facts of organic chemistry.

In the present experiments the benzene and chlorine have been purified as carefully as possible. With the exception of two quantum efficiency determinations the effect of oxygen was not studied. Even in these two runs the amount of oxygen was relatively small and its effect not marked. It is quite possible that a different type of reaction would have been ob-

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(7) Leighton and Forbes, THIS JOURNAL, 52, 3139 (1930).

served with larger amounts of this gas. In a few preliminary runs the effect of water vapor was found also not to be very marked.

Previous studies on the chlorination and bromination of benzene under the influence of radiation have been carried out largely either in liquid benzene or in benzene dissolved in some solvent.[8,9,10,11,12,13] In these studies it either has been shown or assumed that the main product in the chlorination is benzene hexachloride ($C_6H_6Cl_6$). In the bromination both phenyl bromide and benzene hexabromide have been found. In the present work it has been shown that both substitution and addition take place and that as many as nine molecules of chlorine may react with one benzene molecule in the limit to give dodecachlorocyclohexane (C_6Cl_{12}). It is known that α-benzene hexachloride reacts slowly or not at all with chlorine.[14] Therefore either the α modification is not formed in the present work or it will react with chlorine atoms on the walls of the vessel. It seems more probable that when a small amount of benzene is present in a large excess of chlorine containing chlorine atoms, simultaneous addition and substitution take place at all stages of the reaction and it would be hopeless to try to isolate any one substance in the pure form until the reaction is complete. As shown in the previous work[1] if the chlorine is not in large excess benzene hexachloride will be one of the main products, although as judged by the melting point the α modification is not the principal one formed.

There are two simple ways in which chlorine atoms might react with benzene

$$Cl + C_6H_6 = C_6H_5Cl + H \qquad (15)$$
$$Cl + C_6H_6 = C_6H_5 + HCl \qquad (16)$$

These would be followed by either

$$H + Cl_2 = HCl + Cl, \text{ or} \qquad (17)$$
$$C_6H_5 + Cl_2 = C_6H_5Cl + Cl \qquad (18)$$

Reaction (15) is exoenergetic. This is probably also true of (16). Chains leading to substitution might be initiated either way providing neither has too high a heat of activation. The experiments indicate, however, that substitution is relatively unimportant at the start of a run (at least at 25°), so that it seems doubtful whether either (15) or (16) takes place to any large extent in the present experiments. Attempts have been made to estimate heats of activation for (15) and (16) by the methods of Eyring and Polanyi[15] and of Eyring.[16]

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(8) Slator, *Z. physik. Chem.*, **45**, 540 (1903).

(9) Luther and Goldberg, *ibid.*, **56**, 43 (1906).

(10) Bodenstein, *ibid.*, **85**, 329 (1913), has estimated the quantum efficiency for the chlorination to be very high.

(11) Meidinger, *ibid.*, **5B**, 29 (1929).

(12) Rabinowitsch, *ibid.*, **19B**, 190 (1932).

(13) Alyea, THIS JOURNAL, **52**, 2743 (1930), finds the yield per ion pair in the reaction induced by alpha particles to be very high.

(14) *Cf.* Mathews, *J. Chem. Soc.*, **59**, 166 (1891).

(15) Eyring and Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

(16) Eyring, THIS JOURNAL, **53**, 2537 (1931).

As first approximations the reactions C–H + Cl = C + H–Cl and C–H + Cl = C–Cl + H were studied. The necessary constants for evaluating approximate Morse functions for the Franck–Condon curves for C–H and H–Cl molecules are known.[17] For C–Cl the value of r_0 (the equilibrium distance between centers) was assumed to be 1.8 Å.[18] and ω (the first constant in the equation for vibration levels) was taken as 712 cm.$^{-1}$.[19] The values of the energies of activation are sensitive to the assumed ratio of coulombic to interchange binding. If 0.1 is taken for all three molecular species, the calculated heat of activation for the first reaction (C–H + Cl = C + H–Cl) is about 26 kcal., while this is lowered considerably if a higher value for this ratio is assumed. About all one may predict with certainty concerning this reaction is that the heat of activation is probably higher than for the reaction Cl + H–H = H–Cl + H which is involved in the hydrogen–chlorine reaction. For the other reaction (with formation of C–Cl and H) the calculations lead one to expect the formation of a stable complex. It is possible to estimate roughly the effect of other parts of the benzene molecule on these activation energies[20] but the accuracy of the calculations would leave something to be desired. From a theoretical standpoint one is not justified in excluding either reaction (15) or (16), although little can be said concerning their probability. It is possible that the larger amount of substitution at 35° than at 25° may be due to the high heat of activation of (18).

It has been shown recently by Ritchie and Norrish[21] that the hydrogen–chlorine reaction follows the same type of equation as that obeyed by the hydrogen–bromine reaction.[22] In both reactions the chains may be stopped largely by the recombination of halogen atoms although other chain-stopping steps are conceivable. Recently Leermakers and Dickinson[23] have studied the photochlorination of tetrachloroethylene in carbon tetrachloride solution. These authors find the rate to be proportional to the square root of the intensity absorbed and to the chlorine concentration. They state that a satisfactory rate equation may be derived in several ways. In particular one may assume either a triatomic chlorine molecule, Cl_3,[24] or an intermediate free radical C_2Cl_5. Dickinson and Leermakers[25] have shown that a sensitized reaction between oxygen and tetrachloroethylene takes place when oxygen is present.

Since the substitution reaction should lead to no pressure change the

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(17) *Cf.* Kimball and Eyring, THIS JOURNAL, **54**, 3876 (1932); Jevons, "Report on Band Spectra of Diatomic Molecules," The Physical Society, London, 1932, p. 274.

(18) Pierce, *Phys. Rev.*, **43**, 145 (1933).

(19) Harkins and Bower, *ibid.*, **38**, 1845 (1931).

(20) *Cf.* Eyring, THIS JOURNAL, **54**, 3191 (1932).

(21) Ritchie and Norrish, *Proc. Roy. Soc.* (London), **A140**, 99, 112 (1933).

(22) Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **121**, 127 (1926).

(23) Leermakers and Dickinson, THIS JOURNAL, **54**, 4648 (1932).

(24) Rollefson and Eyring, *ibid.*, **54**, 170 (1932).

(25) Dickinson and Leermakers, *ibid.*, **54**, 3852 (1932).

empirical equation (13) which accounts fairly satisfactorily for the rate of total pressure change at the beginning of a run should be dependent entirely on the addition reaction. There are several different ways in which this equation may be derived. One may assume either Cl_3 molecules, or an intermediate complex C_6H_6Cl or a three-body collision between a chlorine atom, a chlorine molecule and a benzene molecule. All of these methods are equivalent to postulating an intermediate compound of the formula $C_6H_6Cl_3$ which may have a mean life comparable to the duration of a collision or much longer. With this in mind one may write the equations

$$Cl_2 + h\nu = Cl({}^2P_{1/2}) + Cl({}^2P_{3/2});\ +d(Cl)/dt = k_1I_a \tag{19}$$

$$Cl + Cl_2 + C_6H_6 = C_6H_6Cl_3;\ +d(C_6H_6Cl_3)/dt = k_2(Cl)(Cl_2)(C_6H_6) \tag{20}$$

$$C_6H_6Cl_3 = C_6H_6Cl_2 + Cl;\ -d(C_6H_6Cl_3)/dt = k_3\,(C_6H_6Cl_3) \tag{21}$$

$$C_6H_6Cl_3 = C_6H_6 + Cl_2 + Cl;\ -d(C_6H_6Cl_3)/dt = k_4(C_6H_6Cl_3) \tag{22}$$

$$Cl + Cl = Cl_2;\ -d(Cl)/dt = k_5(Cl)^2 \tag{23}$$

It follows that

$$\begin{aligned} +d(C_6H_6Cl_2)/dt &= (k_1I_a/k_5)^{1/2}(k_2k_3/(k_3 + k_4))(Cl_2)(C_6H_6) \\ &= -K\,dP/dt \end{aligned} \tag{24}$$

where I_a is the intensity of the absorbed radiation. Equation (26) is identical with equation (13) in form. There should, perhaps, be included in k_5 a term dependent on the total pressure since the recombination of chlorine atoms would probably take place as the result of a three-body collision.

While equation (24) accounts satisfactorily for the observed rate of change of total pressure at the beginning of a run, it contains no step in its derivation which leads to the formation of hydrogen chloride. Neither does it account for the rate of disappearance of chlorine during the course of a run.

The fact that substitution takes place to a very small extent at the beginning of a run may be explained in one of the following ways. (1) An intermediate compound may be formed which slowly splits out hydrogen chloride. This would be in accord with mechanisms frequently postulated in organic chemistry. (2) The addition compounds ($C_6H_6Cl_2$, $C_6H_6Cl_4$ and $C_6H_6Cl_6$) may react with chlorine atoms (probably on the walls) to form hydrogen chloride, the resulting free radicals then reacting with molecular chlorine. That reactions of this type must occur is indicated by the nature of the ultimate product which is formed on complete chlorination of benzene. (3) A condensed layer may form on the walls which would dissolve some of the benzene and the substitution reaction may take place entirely in this layer. (4) Reactions (15) and (16) may simply be slow compared to the addition reaction.

There was usually a small but definite decrease in pressure after turning off the mercury arc lamp providing this was done before the reaction had proceeded too far. This did not continue indefinitely. This indicates that the first addition compound ($C_6H_6Cl_2$) adds chlorine in t according to the equation

$$C_6H_6Cl_2 + 2Cl_2 = C_6H_6Cl_6 \qquad (25)$$

Reaction (25) is in accord with well-known facts of organic chemistry concerning molecules with conjugated double bonds.

No reference to dichlorocyclohexadiene ($C_6H_6Cl_2$) could be found excep in textbooks which give it as an intermediate in the production of benzene hexachloride. The only compound of this empirical formula mentioned is 3,5-dichloro-1,2-dihydrobenzene,[26] which is almost certainly not the first compound formed when chlorine adds to benzene. It has been shown, however, that α-benzene hexachloride loses hydrogen chloride upon heating to form 1,2,4-trichlorobenzene.[27] Whether $C_6H_6Cl_2$ would lose hydrogen chloride easily is problematical. It is impossible to estimate the heat of the reaction $C_6H_6Cl_2 = C_6H_5Cl + HCl$ precisely, but a crude calculation shows that it would probably be endothermic, perhaps to the extent of 30 kcal. It seems very doubtful, therefore, whether this reaction could account for the amount of substitution actually observed, although it would undoubtedly have a high temperature coefficient.

It seems probable, therefore, that the main initial reaction is addition according to equation (21), accompanied by small amounts of either (15) or (16). It is possible that the substitution might take place by means of the complex $C_6H_6Cl_3$, *viz.*, $C_6H_6Cl_3 = C_6H_5Cl + HCl + Cl$. If most of the chlorine atoms form Cl_3 this mechanism would be quite plausible unless one wishes to postulate that chlorine atoms and Cl_3 are both present in appreciable quantity and react with benzene in different manners. No definite proof exists for such an assumption.

The increased amount of substitution with increasing temperature finds a ready explanation in the temperature coefficients of the substitution reactions, whereas the slower rate of disappearance of chlorine at the higher temperature is due in part to the smaller amount of reaction (25). It is possible also that the rate of recombination of chlorine atoms will be increased considerably by an increase of temperature.

A further discussion of theoretical aspects of chlorination will be given at a later date when data on chlorination of phenyl chloride are published.

One of the authors (H. P. S.) held the Herbert W. Rice fellowship during 1930–31 and a Jesse Metcalf fellowship during 1931–32.

Summary

1. The photochemical chlorination of benzene in the gas phase proceeds by a short chain reaction.

2. The rate of pressure change at the beginning of the reaction is pro-

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(26) Crossley and Haas, *J. Chem. Soc.*, **83**, 501 (1903).

(27) Sho-e Tei and Shigeru Komatsu, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **10A**, 325 (1927).

portional to the square root of the light intensity, the pressure of the chlorine and the pressure of the benzene.

3. Both addition and substitution take place, but the main initial reaction is addition.

4. The mechanism of the reaction has been discussed.

PROVIDE , RHODE ISLAND

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Actinometry with Uranyl Oxalate at λλ 278, 253 and 208 mμ, Including a Comparison of Periodically Intermittent and Continuous Radiation

BY F. PARKHURST BRACKETT, JR., AND GEORGE S. FORBES

Following several investigations by others of the photolysis of uranyl oxalate, W. G. Leighton and one of us[1] determined quantum yields, ϕ, in monochromatic light at each of nine wave lengths, and urged a wider use of the reaction for purposes of actinometry. An identical value of ϕ, 0.59 (λ = 313 mμ) at comparable concentrations, has been obtained by Heidt and Daniels.[2] Using a zinc spark, we have now measured quantum yields at 208 mμ. Also by redetermining ϕ at 278 and 253 mμ, we were able to compare the relative efficiencies of periodically intermittent and continuous radiation, a question already investigated by Lazareff and Perrin[3] with dyestuffs in polychromatic light, but well worthy of additional study if uranyl oxalate is to be used for actinometry.

We used a spark apparatus[4] maintaining constant intensity within a few per cent. for two hours, and simpler than that described by Boas.[5] The monochromator[4] with its train of crystal quartz was used without change. Including so far as possible only λλ 206 and 210 mμ, 16,000 ergs/sec. were available at the exit slit, at λ 253 mμ 30,000 ergs/sec., at λ 278 mμ 14,000 ergs/sec. The fused quartz reaction vessels, 90 mm. high, 40 mm. broad and (1) 5.3 mm. or (2) 5.5 mm. thick, when containing the actinometer solution, completely intercepted and absorbed the highly divergent beam. A motor-driven spiral of flattened platinum wire provided adequate stirring. The system was not thermostated, but the temperature was consistently recorded.

Our radiometric apparatus, as well as our procedure, agreed for the most part with that previously employed in this Laboratory[6,1] and discussed at length by P. A. and W. G. Leighton.[7] The linear thermopile had 20 hot and 20 cold bismuth–silver junctions, and the d'Arsonval galvanometer a sensitivity at 1 meter of 15 mm./microvolt. The system was calibrated against radiometric standards C39, 69 and 154 following directions of the Bureau of Standards. As results were not wholly concordant, these lamps were recalibrated by the Bureau. Certain consistent discrepancies in these results as well as those of earlier intercomparisons are explained in the report from the Bureau as due to defects in the filaments of C69 and C154, possibly acquired in shipment. Both of these lamps have been retained at the Bureau, as they are apparently unsuited for quantitative work. The third standard, C39, was returned to us with a new certificate which shows but little change from the original standardization. Consequently final computations have now been based upon it, using the two certificates furnished by the Bureau.

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(1) Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930); with bibliography.

(2) Heidt and Daniels, *ibid.*, **54**, 2384 (1932).

(3) Lazareff and Perrin, *Compt. rend.*, **177**, 1436 (1923).

(4) Forbes and Brackett, THIS JOURNAL, **53**, 3973 (1931).

(5) Boas, *Z. Physik*, **60**, 690 (1930).

(6) P. A. Leighton and G. S. Forbes, THIS JOURNAL, **51**, 3549 (1929)

The four lines of the group 203–214 mμ were well resolved and widely separated on the focal plane. Also, the total variation of ϕ over the actinic region is small. Therefore errors due to false light became less serious. We interposed successively (1) plates transmitting infra red only, (2) Pyrex, (3) layers of uranyl oxalate, and showed that radiation having the mean wave length λ 208 mμ included not more than 1% of non-actinic light. The combination of radiations λλ 203 and 214 mμ would tend to behave as λ 208 mμ. The radiation designated as of λ 253 mμ was of the same order of purity, but that at λ 278 mμ was only 92% actinic, and included some visible light. A large part of the contaminations was transmitted, and after radiometric evaluation was subtracted from the total.

Materials.—Uranyl sulfate, $UO_2SO_4 3 \cdot H_2O$ (Kahlbaum, purity not specified), was thrice recrystallized and centrifuged while washing the crystals with small amounts of water. Oxalic acid (Mallinckrodt reagent) was twice treated in the same fashion. Professor Grinnell Jones kindly furnished water from his Kraus conductivity still for purification of materials and for making up solutions. Stock solutions were stored in bottles of resistant glass, enamelled black on the outside.

Analytical.—The procedure developed by W. G. Leighton[1] was followed in detail, and fixed the end-point within 3×10^{-7} oxidation equivalents of permanganate. Samples of actinometer solution contained 3×10^{-4} equivalents of oxalic acid, of which 5–10% was decomposed by light. This photolyzed portion was determined within 2–3%. No measurable dark reaction occurred.

Computations.—The equation for calculating total energy, E_a, absorbed during a photolysis followed the principle developed by W. G. Leighton and Forbes.[8] These authors based their calculations upon the light transmitted by the rear window of the reaction vessel, while we,

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(7) P. A., and W. G. Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

(8) Ref. 1, p. 3143.

confronted by much higher absorptions, had to start behind the front window. We include, however, the case of incomplete absorption.

$$E_a = \rho\pi dRQ\Sigma[t(\Sigma B)_{av}]\left[1 - \frac{\Sigma \mathbf{B}}{\Sigma B}\frac{1}{1 - r_3}\right]$$

Here E_a is in quanta. ρ corrects for slow variations in the sensitivity of the radiometer obtained by taking galvanometer readings several times during each run while irradiating the thermopile with a carbon filament lamp operated under fixed electrical conditions and frequently compared with C39. π is a factor experimentally determined to allow for the resistance pattern in the thermopile-galvanometer circuit which lowered its sensitivity. This pattern has been discussed previously.[9] d is an experimentally determined factor combining corrections for oblique incidence at the extreme edges of the beam emergent from the exit slit upon the thermopile window and junctions, also for the very small amount of radiation not intercepted by the hot junctions under such circumstances. $R = (1 - r_1)(1 - r_3)/(1 - r_2)$ where $(1 - r_1)$ is the fraction of energy transmitted by the crystal quartz window of the thermopile exposed to the entire radiation of a carbon lamp. The Bureau certificates give $r_1 = 0.085$. At the wave length λ, the transmission (experimentally determined) of the same window is $(1 - r_2)$ as noted in Table I. The quantity $(1 - r_3)$ refers to the front window of the reaction vessel in the above formula, determined as indicated below.

TABLE I

λ, mμ	$(1 - r_2)$	Investigators
313	0 897	Leighton and Forbes
278	.888	Interpolated
254	880	Leighton and Forbes
208	.831	Forbes and Brackett

The crystal quartz plate used at 208 mμ was lent by Professor Theodore Lyman. The transmission of the front window (in contact with solution) was taken as the square root of the over-all transmission of the reaction vessel filled with water and measured at λ, but first corrected for the absorption of 5 mm. of water according to Kreusler.[10] We later determined directly, in air, the transmission of the front window (after removing the back window) at 208 mμ. Recalculating to air–quartz–water transmission, the square root of the over-all transmission was duplicated within 2%.

TABLE II

λ, mμ	Cell	$1 - r_3$	R	$1/(1 - r_3)$
278	2	0.951	0.980	1.051
253	1	.941	.979	1 04
253	2	.933	.970	1.072
208	1	.91	1.00	1.10
208	2	.879	0.967	1.138

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(9) Ref. 1, p. 3141, also Ref. 7, p 1891.

(10) Kreusler, *Ann. Physik*, **6**, 421 (1901).

$Q = 1.060 \times 10^{11}$ (quanta/erg) at 208 mμ, 1.289 at 253 mμ and 1.416 at 278 mμ. In $\Sigma[t(\Sigma B)_{\text{av.}}]$ the quantity B is an apparent flux corresponding to a given deflection of the galvanometer and obtained from the calibration curve of the thermopile.

The radiant flux of the divergent beam was integrated behind the exit slit by a method similar in principle to that developed in this Laboratory.[11,6,1] But since the beams were narrow, and the position of the spark not wholly constant, the thermopile was moved in steps of 1 mm. across the beam, not 2-mm. steps as practiced frequently[11,6,1] in this Laboratory. $(\Sigma B)_{\text{av.}}$ = average of two successive integrations *without* the reaction vessel in place. t = the time, in seconds, of the photolysis between two successive integrations, during which photolysis was occurring. $\Sigma\mathbf{B}$ = a summation to be made behind the reaction vessel about half way through the photolysis. $\frac{\Sigma \mathrm{B}}{\Sigma B}\cdot\frac{1}{1 - r_3}$ = the fraction of the energy entering the solution which emerges from the reaction vessel, where $(1 - r_3)$ now refers to the *back* window, equal to $(1 - r_3)$ for the front window, as shown above.

It can be shown that the equation for evaluation of E_a corrects for any energy flux reflected from the rear window back into the cell, there to be reabsorbed by the solution. At wave lengths where 25% or more of incident light passes the rear window, a further correction for incomplete absorption of this reflected light is required. In a typical run (No. 12, at 208 mμ) radiometric quantities were as follows

$$\rho = 1.042;\ \pi = 2.91;\ R = 1.001;\ d = 1.003;\ Q = 1.060 \times 10^{11}$$

$$\Sigma[t(\Sigma B)_{\text{av.}}] = 81.62 \times 10^6 \text{ ergs}$$

$$\left[1 - \frac{\Sigma \mathrm{B}}{\Sigma B}\cdot\frac{1}{1 - r_3}\right] = 1 - 0.008 \times 1.10 = 0.991$$

$$E_a = 1.042 \times 2.91 \times 1.001 \times 1.003 \times 1.060 \times 10^{11} \times 81.62 \times 10^6 \times 0.991 = 2.61 \times 10^{19} \text{ quanta}$$

Number of molecules of oxalic acid decomposed = 1.34×10^{19} or 7.3% of the whole. Quantum yield $\phi = 1.34 \times 10^{19}/2.61 \times 10^{19} = 0.514$.

Results.—Table III summarizes all our experiments except the first seven which were discarded as a preliminary series, and a single later experiment during which the apparatus broke down.

The two high results at 253 mμ were weak experimentally, as only four radiometric integrations (reaction vessel removed) were made, and a shifting of the slit during photolysis was suspected as well. In the other series, no results deviate from the average by more than 6%. For computation of averages and of probable errors each experiment was weighted according to the number of integrations.

Table IV compares our results with those of Leighton and Forbes. In calculating $\phi_{25°}$ from $\phi_{28°}$ the ten degree temperature coefficient 1.03 was used.[12]

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(11) Villars, THIS JOURNAL, **49**, 326 (1927).

(12) Ref. 1, p. 3150.

TABLE III

λ, mμ	$H_2C_2O_4$ moles per kg.	UO_2SO_4 moles per kg.	Number of integrations	Quanta absorbed $\times 10^{-19}$	Molecules decomposed $\times 10^{-19}$	Gross yield ϕ
278	0.04853	0.010	15	2.492	1.45	0.583
278	.04853	.010	15	2.789	1.65	.595
278	.04853	.010	11	1.993	1.11	.558
278	.04853	.010	11	1.983	1.22	.615
					Average	0.59 ± 0.01
253	0.04967	0.010	4	1.739	1.13	0.650
253	.04967	.010	4	1.698	0.976	.575
253	.04967	.010	4	1.994	1.40	.704
253	.04967	.010	4	2.023	1.52	.751
253	.04967	.010	12	2.620	1.63	.620
253	.04967	.010	12	2.11	1.25	.593
					Average	0.63 ± 0.03
208	0.04967	0.010	16	2.61	1.34	0.514
208	.04967	.010	14	2.23	1.012	.454
208	.04967	.010	16	2.36	1.15	.488
208	.04967	.010	16	2.51	1.176	.469
					Average	0.48 ± 0.01
208	0.04995	0.030	8	1.56	0.867	0.556
208	.04976	.030	8	1.32	.715	.543
					Average	0.55 ± 0.01
208	0.01963	0.020	7	1.073	0.521	0.486
208	.01963	.020	7	1.11	.594	.534
208	.01963	.020	7	1.010	.564	.560
208	.01963	.020	7	0.959	.497	.520
					Average	0.53 ± 0.01
208	0.05058	0.000	12	1.87	0.067	0.036
208	.05058	.000	11	1.85	.061	.033
208	.05058	.000	11	8.25	.024	.003
					Average	0.02 ± 0.01

TABLE IV

λ, mμ	300	278	265	254	253	208
Forbes and Brackett, 28°		0.59			0.63	0.48
Forbes and Brackett, 25°		0.58			.62	.47
Leighton and Forbes, 25°	0.57		0.58	0.60		

The numerical agreement between the two series is very close considering that two entirely different sets of apparatus were used, and that the periodically intermittent light of the spark was compared with the continuous light of the mercury vapor lamp. A reasonable inference is that equal energies from the two sources, as evaluated by radiometry, are photochemically equivalent within two or three per cent. in this reaction at least. Of course this may mean only that the percentage errors, in integrating the energy, are the same for radiometer and actinometer alike. Forbes, Heidt and Brackett(13) came to identical conclusions regarding the photochemical reaction between quinine and dichromic acid at λ 280 mμ where some experiments were carried out with the mercury vapor lamp and some with the zinc spark. It would be going beyond the evidence to make a more sweeping statement at this time. Lazareff and Perrin,[8] who came to a similar conclusion by photolyzing dyestuffs in polychromatic light, insist upon the reservation that the light commences and ceases to act instantaneously, *i. e.*, that no induction periods or after effects are present. This last point is now of interest in view of an article by Beard and Reiff,[14] who investigated the stability of gasoline in light using an oxalic acid–uranyl *acetate* actinometer, the reaction in which seemed to progress to a slight extent in the dark after exposure to sunlight.

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(13) Forbes, Heidt and Brackett, THIS JOURNAL, 55, 589 (1933). See Fig. 1, curve 4.

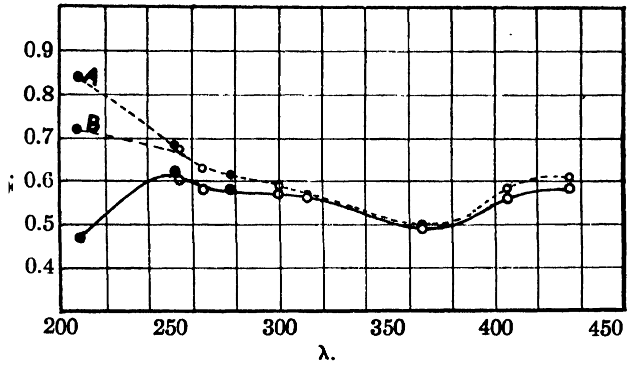

Fig. 1.——Gross yield, - - - - corrected yield. A, if $UO_2C_2O_4$ is the complex; B, if $UO_2(C_2O_4)_2$ is the complex. For a solution 0.05*m* in $H_2C_2O_4$ and 0.01*m* in UO_2SO_4. O, Leighton and Forbes; ●, Forbes and Brackett; temp., 25°. A and B practically coincident at 255 mμ and above.

The (averaged) *gross* quantum yields have been plotted against λ in Fig. 1, which also includes the data of Leighton and Forbes. In addition, corrected yields appear, obtained by apportioning the total light absorbed among the absorbing constituents[15] and substracting (1) the light absorbed by uncombined oxalic acid, (2) the unsensitized photolysis of this uncombined fraction.

At 208 mμ the absorbents were assumed to be (1) $UO_2HC_2O_4^+$ or $UO_2(HC_2O_4)_2$ or $UO_2C_2O_4$ or $UO_2(C_2O_4)_2^-$, (2) UO_2^{++} and UO_2SO_4, (3) uncombined $H_2C_2O_4$, HC_2O_4', $C_2O_4^-$, (4) water (plus H_2SO_4 formed by metathesis) the absorption of which is negligible over the very thin layer where practically all the light is absorbed. Table V gives the numerical values.

The summation $KC = K_1C_1 + K_2C_2 + K_3C_3$ was resolved at 208 mμ as follows: K_2 was found directly for UO_2SO_4 and K_3 for $H_2C_2O_4$. Next

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(14) Beard and Reiff, *Ind. Eng. Chem., Anal. Ed.*, 3, 280 (1931).

(15) Ref. 1, p. 3149.

TABLE V

ABSORPTION COEFFICIENTS AT 208 mμ AND 28°

$10^{-\Sigma(KC)d}$ = transmission as explained above. $d = 0.53$ cm. in each of the given measurements. K of the mixtures has been obtained by dividing (ΣKC) by the original total concentration of uranyl sulfate.

Uranyl sulfate	Oxalic acid	$10^{-\Sigma(KC)d}$	K
0.00025	...	0.48	2.41×10^3
....	0.0005	.46	1.27×10^3
.00002	.0001	.75	1.20×10^4
.0002	.001	.058	1.17×10^4
Average for uranyl oxalate solutions where [oxalic acid] = $5[UO_2SO_4]$			1.18×10^4

TABLE VI

ABSORPTIONS AND NET QUANTUM YIELDS AT 208 mμ, $t = 28°$

Total uranyl	Total oxalate	ϕ_{gross}	K_1*	K_1C_1*/ ΣKC	K_3C_3*/ ΣKC	$\phi_{\text{corr.}}$*	K_1**	K_1C_1**/ ΣKC	K_3C_3**/ ΣKC	$\phi_{\text{corr.}}$**
0.01	0.05	0.48	6.9×10^3	0.55	0.44	0.84	8.2×10^3	0.65	0.34	0.72
.03	.05	.55	6.9×10^3	.67	.19	.67	8.2×10^3	.80	.07	.59
.02	.02	.53	6.9×10^3	.62	.13	.61	8.2×10^3	.73	.02	.54

* If the complex contains one oxalate ion; ** if complex contains two oxalate ions.

C_1 and C_2 were calculated from data of Leighton and Forbes at 313 mμ where K_1 can be found directly because K_3C_3 is negligible even in the presence of large excess of oxalic acid. Given C_1, we found C_3 by subtracting C_1 from total oxalate, assuming the complex to be $UO_2C_2O_4$, or by subtracting $2C_1$, assuming it to be $UO_2(C_2O_4)_2^{-}$. Substituting C_1, C_2, C_3, K_2, K_3 in the original equation, alternative values of K_1 were found, and the absorption fractions $K_1C_1/\Sigma KC$. . . resulted. Finally $\phi_{\text{corr.}}$ was calculated excluding light absorbed by the uncombined oxalic acid, correcting also for the oxalate decomposed by the light absorbed by the oxalic acid itself (see Table III, last series). The equation is

$$\phi_{\text{corr.}} = \frac{\phi_{\text{gross}} - \phi_{H_2C_2O_4}\,(K_3C_3/\Sigma KC)}{(\Sigma KC - K_3C_3)/\Sigma KC}$$

At wave lengths greater than 208 mμ, $\phi_{H_2C_2O_4}$ rapidly approaches zero.

Further work to determine the formula of the photolyte and the reason for less efficient utilization of absorbed quanta in the presence of uncombined uranyl ion is in progress in this Laboratory.

In using our gross yields (in the vicinity of 25°), for purposes of actinometry, corrections must be made for the reflection (and very possibly absorption) by the front window of the cell actually used. At 208 mμ the optical properties of various quartz plates differ surprisingly even when identical in the visible and longer ultraviolet. Employing the concentrations specified above, transmission and reflection at the rear window are negligible unless the layer is less than 1 mm. thick. Temperature fluctuations, unless extreme, are unimportant. Efficient stirring is indispensable.[16]

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[16] Compare Ref. 1, p. 3148 and THIS JOURNAL, 52, 5309 (1930), noting that the letters B and C should be interchanged on the graph (only).

Summary

The gross quantum yield, ϕ_{gross} at 27 ± 2° in molecules of oxalic acid per quantum, in the photolysis of a solution in which $[UO_2SO_4] = 0.01$ and $[H_2C_2O_4] = 0.05$ is 0.48 ± 0.01, $\lambda = 208$ mμ; 0.63 ± 0.03, $\lambda = 253$ mμ; 0.59 ± 0.01, $\lambda = 278$ mμ. After correction for light absorbed by uncombined oxalic acid, and for the unsensitized photolysis of this acid, the quantum yield, when $\lambda = 208$ mμ, is considerably higher than at the lower frequencies. A zinc spark of high constancy was the light source. Elaborate radiometric and analytical precautions were taken.

The various absorption coefficients involved are given.

Owing to accentuation of radiometric difficulties in the region of 208 mμ, the uranyl oxalate actinometer should now be especially valuable for photochemical work in this part of the spectrum. The necessary precautions are emphasized.

ϕ_{253} and ϕ_{278} agree closely with findings of W. G. Leighton and one of us in the same regions. It is thus indicated that the two thermopiles used and the uranyl oxalate actinometer integrate periodically intermittent and constant radiation in equivalent fashion.

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Fluorine Polyhalides of Organic Amines

BY HAROLD SIMMONS BOOTH, WILLIAM C. MORRIS AND G. D. SWARTZEL

In this communication are described the preparation and properties of the compounds formed by the union of iodine trichloride and typical members of the four classes of substituted ammonium fluorides and pyridine fluoride. These prove to be similar in general properties to the corresponding fluorine polyhalides of the alkali metals and ammonium,[1] and the trihalides[2] and pentahalides[3] of substituted ammonium salts.

The salts here described were prepared by one of the methods recently developed[1] for the analogous alkali metal and ammonium salts involving the addition of iodine trichloride to the fluoride of the base.

The fluorides of the organic amines are best made by adding slightly more than an equivalent of aqueous hydrofluoric acid to the amine. Iodine trichloride is conveniently prepared by adding finely powdered iodine to an excess of liquid chlorine cooled by solid carbon dioxide in acetone. On evaporating the excess of chlorine the pure iodine trichloride remains as a fluffy powder which is very easily handled.

A cold saturated aqueous solution of this reagent on addition to a cold, nearly

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(1) Booth, Swinehart and Morris, THIS JOURNAL, 54, 2561 (1932); *J. Phys. Chem.*, 36, 2279 (1932).

(2) Cremer and Duncan, *J. Chem. Soc.*, 133, 1857 (1931).

(3) Chattaway and Hoyle, *ibid.*, 123, 654 (1923).

saturated, slightly acidified solution of the fluoride of the amine causes the immediate separation of the bright yellow fluorine iodine trichloride salt. The compounds described below all form brilliant yellow needle-like tetragonal prisms which exhibit parallel extinction under crossed nicols in two positions and are isotropic in the third. They were collected on a Jena glass filter and dried centrifugally.

Analysis.—For analysis the sample was dissolved in a slight excess of sodium hydroxide solution and gently boiled until colorless, cooled and a small amount of hydrogen peroxide solution added to reduce any hypochlorite and hypoiodite to the normal halide. Excess hydrogen peroxide was driven off by boiling, the solution again cooled and acidified with dilute sulfuric acid, and a small amount of sulfurous acid added to reduce any free iodine. The excess sulfur dioxide was driven off by boiling, a small amount of nitric acid and a slight excess of one-tenth normal silver nitrate solution added and the solution boiled. The mixed silver iodide and chloride was then filtered, washed, dried and weighed on a Jena glass filter. The excess silver nitrate was then back titrated with one-tenth normal ammonium thiocyanate. The following equations give the percentage of iodine and chlorine

$$\mathrm{Cl} = \frac{[0.091035\,(\text{no. m. e. AgNO}_3) - 0.38771\,(\text{wt. Ag salt})] \times 100\%}{\text{weight of sample}}$$

$$\mathrm{I} = \frac{[1.3878\,(\text{wt. Ag salt}) - 0.19894\,(\text{no. m. e. AgNO}_3)] \times 100\%}{\text{weight of sample}}$$

This method of analysis is just as accurate and much quicker than the method of Gooch previously used. The nitrogen was determined by the Kjeldahl method.

The specific properties and analytical results are given in the table. When heated in open melting point tubes the salts undergo decomposition; this appears not to take place in sealed tubes, indicating the phenomenon to be primarily dissociation, analogous to the action of heat on the fluorine polyhalides of the alkali metals.

TABLE I

	Salt	M. p., °C. Open tube	M. p., °C. Closed tube	Sp. gr.
1	$CH_3NH_3FICl_3$	25–30 dec.	35–40	1.216 (4°)
2	$(C_2H_5)_2NH_2FICl_3$	50; dec. 85	60–63	1.216 (19°)
3	$(CH_3)_3NHFICl_3$	116, dec. complete at 140	121–145	1.115 (19°)
4	$(CH_3)_4NFICl_3$	265–267 dec. complete at 275	267–270, dec. 310	1.646 (19°)
5	$C_6H_5NHFICl_3$	175–180; darkens 135	187–190; reddens at 147 no decomp.	2.912 (19°)

	Analyses, % Cl Calcd.	Cl Found		I Calcd.	I Found		N Calcd.	N Found	
1	37.15	37.35	37.25	44.33	43.53	43.48	4.89	4.87	4.88
2	32.59	32.61	32.61	38.89	38.82	38.82	4.29	4.34	4.33
3	34.05	34.06	34.02	40.63	40.53	40.60	4.49	4.47	4.48
4	32.59	32.47	32.51	38.89	38.85	38.77	4.29	4.27	4.28
5	32.00	32.04	32.16	38.19	37.76	37.88	4.22	4.21	4.23

Attempts to prepare analogous compounds from the hydrofluorides of aniline, *m*-nitroaniline and *o*-chloroaniline failed; chlorination obviously occurred, with evolution of heat and acid fumes, and only tarry products were obtained.

Summary

Organic amines form fluorine polyhalides, similar to those formed by the alkali metals, on adding a cold saturated solution of iodine trichloride to a cold saturated solution, slightly acidified, of the hydrofluoride of the amine, except in cases where the amine is chlorinated by the iodine trichloride.

The tetramethylammonium fluoride iodine trichloride is the most stable and the monomethylamine salt the least. The pyridine salt is next in stability to the quaternary amine salt and both of them compare favorably with the corresponding alkali metal polyhalides. The thermal decomposition is primarily dissociation as in the case of the alkali metal polyhalides.

All the organic fluoride polyhalides thus far prepared form orange-yellow tetragonal crystals.

Cleveland, Ohio

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[Contribution from the Metcalf Chemical Laboratory, Brown University]

The Sorption of Oxygen by Nickel Catalysts[1]

By W. Walker Russell and Leonard G. Ghering

In a recent investigation[2] it was found that catalytically active nickel strongly sorbed large amounts of oxygen at 0°. Because evidence of the true nature of a sorption process is probably best obtained by studying it at several temperatures, measurements in the present work have been extended below and somewhat above 0°. Furthermore, sorption measurements have been made on nickel catalysts in several states of activity, in an endeavor to throw further light upon the general problem of the correlation of sorptive behavior with catalytic activity.

Apparatus and Experimental Method

Apparatus.—Although the apparatus shown in Fig. 1 is almost self-explanatory, attention may be called to certain of its features. Catalyst bulb A allowed for successive reductions *in situ*. The manometer M could be used to measure pressures both in the catalyst system A, B, C, D and in the constant volume buret I, J. The by-pass G[3] facilitated the admission of oxygen to the catalyst. Mercury levels were adjusted at the fixed contacts D, E or F by means of a suitably connected radio loud speaker. These settings were reproducible to better than 0.02 mm., the sensitivity of the cathetometer used in the pressure measurements. A diffusion pump backed by a Sprengel pump allowed desorbed gases to be collected. The catalyst was protected by a liquid air trap and trap B. The following baths were employed: ice, 0°; solid ammonia, −78 ± 0.3°; liquid air, −190 ± 3°. A copper–constantan thermocouple showed the constancy of the baths.

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[1] From a thesis submitted in May, 1933, by Leonard G. Ghering to the Graduate School in partial fulfilment of the requirements for the degree of Master of Science.

[2] Russell and Bacon, This Journal, 54, 54 (1932).

[3] Benton and White, *ibid.*, 52, 2325 (1930).

Preparation and Purification of Gases.—These operations were carried out as already described.[3]

Preparation of Catalysts.[2]—The pure nickel catalysts Ni II and VI which weighed 12.12 g. and 20.73 g., respectively, were reduced at 300°. The promoted nickel catalysts Ni III and VII which weighed 7.47 g. and 17.80 g. were reduced at 300 and 350°, respectively. Between measurements, irreversibly held oxygen was removed from Ni VI and VII by again reducing *in situ*, at 300° for the former and at 250° for the latter. Such oxygen was not removed from Ni II and III, but successive surfaces were "regenerated"[3] by heating *in vacuo* at 300° for four hours.

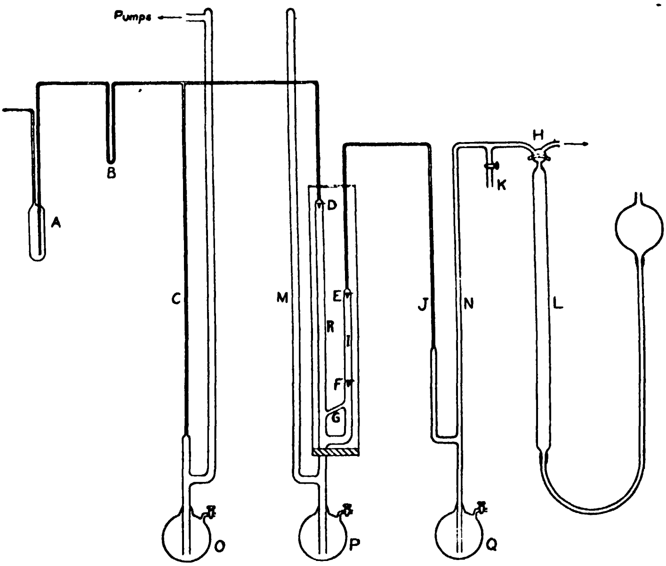

Fig. 1.—Apparatus.

General Procedure in Sorption Measurements.—The reduced catalyst was evacuated at the temperature of reduction continuously for twenty-four hours in order to remove sorbed hydrogen. About 2 mm. pressure of helium was then admitted to ensure temperature equilibrium. With the first increment of oxygen to show a persistent pressure, readings were extended over four hours or more and finally the pressure was built up to about 100 mm. Reversibly adsorbed oxygen was then pumped off in measured increments. Free space values were obtained with helium.

Experimental Results

A. Isotherms.—At liquid air temperature, even on the most inactive surfaces studied, at least 50% of the oxygen sorbed in four hours at a pressure of 80–100 mm. was taken up as fast as diffusion could occur in the apparatus, and with zero pressure, *i. e.*, less than 0.0001 mm. On very active surfaces at room temperature this figure was over 90%. After a persistent oxygen pressure appeared in the system, instantaneous sorption was always followed by a drift which was practically independent of the pressure above 10 mm., but which was larger the higher the temperature and the more active the surface. The forms of the drift curves were very similar to those obtained with hydrogen on zinc oxide in a higher temperature range by others.[4] While the rate of slow sorption on Ni VII during the fourth hour was only 0.05 cc. at −190°, it was twice as great at −78°, eight to nine times as large at 0° and amounted to 0.6 cc. at 24°. Therefore, although equilibrium could be closely approached in four hours at −19°, this was not true at the higher temperatures. However, in no case could oxygen which was slowly sorbed be pumped off at the temperature of sorption. Furthermore, it was found that an isotherm obtained at a given time coincided exactly with one obtained several hours later, if a correction was made for the drift which intervened. It is clear, therefore, that the experimental isotherms shown in Fig. 2 will not differ in shape from equilibrium isotherms but may lie below the latter. Because of the longer times of observation, *i. e.*, Curve 7 (twenty hours), Curve 8 (seven days), and the lesser activity of the surfaces, only Curves 2, 3 and 4 do not represent substantial equilibrium. While in the successive reductions the sorptive capacity of Ni VII could be reproduced to better than 0.5%, Ni VI

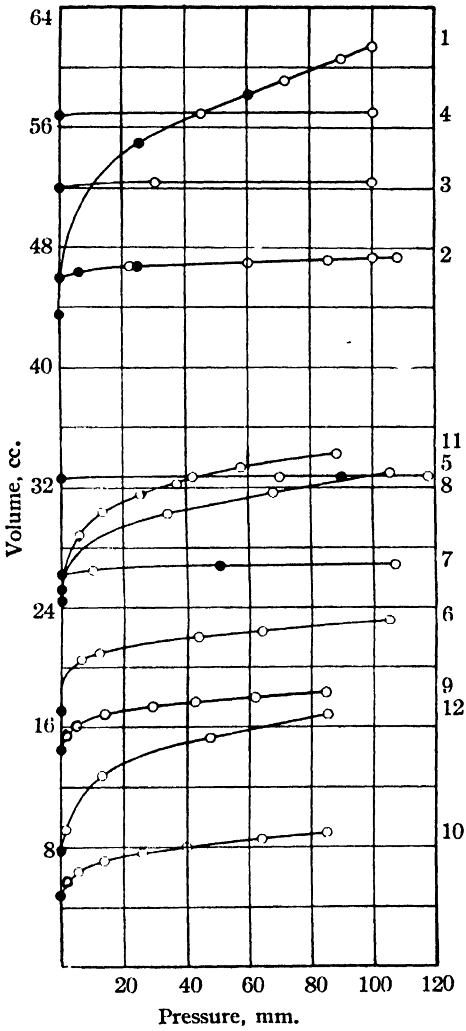

Fig. 2.—Total sorption isotherms. Ni VII: Curve 1, −190°; Curve 2, −78°; Curve 3, 0°; Curve 4, 24°. Ni VI: Curve 5, −190°; Curve 6, −190°, sintered; Curve 7, −78°; Curve 8, 0°. Ni II: Curve 9, −190°; Curve 10, −190°, first regenerated surface. Ni III: Curve 11, −190°; Curve 12, −190°, first regenerated surface. Curves 2, 3 and 4 do not represent equilibrium. Other curves are very near to equilibrium.

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[4] Taylor and Sickman, This Journal, 54, 610 (1932).

was sintered at first rapidly and then at a slow linear rate. Because of this sintering, it was considered that isotherms obtained on the original surface would best illustrate the behavior of Ni VI, *i. e.*, pure active nickel, even though at −78° and above, oxygen sorbed at lower temperatures was present. For like reasons Curves 5 to 12, inclusive, were obtained in this unusual manner which, as will be shown later, has the effect of displacing these isotherms somewhat upward. The reversibility of the sorption depending upon pressure is evidenced by the fact that the open circles (sorption) and the black circles (desorption) lie on the same smooth curves. While at −190° none of the isotherms appear to approach saturation, at 0° and above total sorption becomes almost entirely independent of pressure. A comparison of Curves 1, 2 and 3 with 5, 7 and 8, and also 11 with 9 brings out the function of the promoter in increasing the extent of surface, and, due to the relatively smaller weights of the promoted catalysts, such a comparison is conservative. The larger weights of Ni VI and VII should also be kept in mind. The effect of the first regeneration of Ni III and II was to displace Curves 11 and 9 without distortion downward to new positions as Curves 12 and 10. Sintering Ni VI for 124 hours at 300° has caused the decrease in total sorption shown by the relative positions of Curves 5 and 6.

B. Isobars.—The isobars for sorptions at 100 mm. pressure at the end of four hours, shown in Fig. 3, serve to emphasize certain characteristics of sorptive behavior. Because of the short time allowed, it is clear that the points at the higher temperatures do not represent equilibrium. Some idea of the difference which this makes can be had by comparing Curves 5 and 6, since the latter is an equilibrium curve. The isobars for Ni VI are unusual in the sense already discussed under isotherms. While the total sorption, in general, at first decreased with rising temperature, passing through a minimum near −78° and then increasing, that on the regenerated surfaces showed the initial decrease, but little change above −78°. Unlike sintering, regenerating a surface caused no change in its reversible adsorption. On all surfaces the reversible adsorption decreased sharply above −190° and became very small near 0°. As a result the irreversible adsorption, except on the regenerated surfaces, increased with temperature, and at an accelerating rate. The term reversible adsorption as used here designates oxygen which can be desorbed by pumping at the temperature of sorption. By irreversible adsorption is meant the difference between the experimentally determined total and reversible adsorptions.

Because of the unusual method of obtaining the isobars for Ni II, III and VI, the effects of heating a surface carrying sorbed oxygen could be directly observed. When a surface initially saturated with oxygen at −190 or −78° was heated to −78 or 0°, some of the reversibly adsorbed oxygen was desorbed. Only if the surface was relatively inactive, *e. g.*, regenerated, or if it was evacuated prior to heating, was irreversibly adsorbed oxygen observed to be appreciably desorbed. Due to the rapid drift setting in near 0°, desorption amounted to less than 0.5 cc. on Ni VII, and a permanent decrease in irreversible adsorption was found only on the regenerated surfaces.

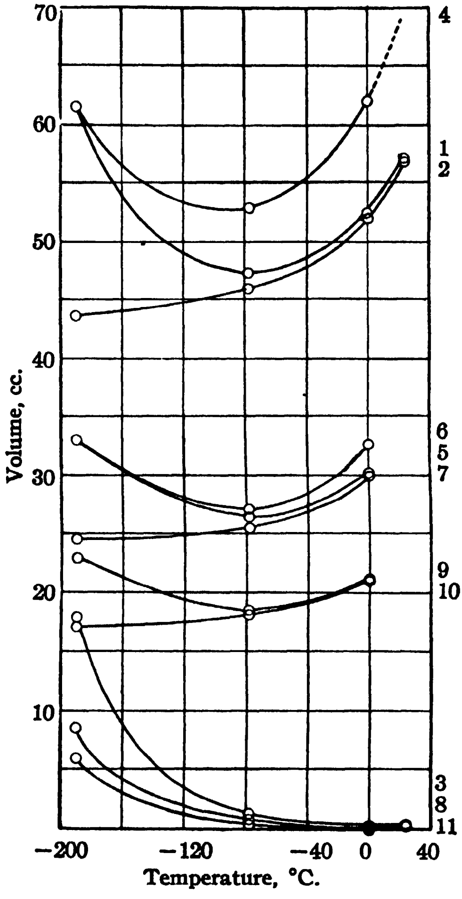

Fig. 3.—Isobars, at 100 mm., for amounts sorbed in four hours. Abbreviations: T. S., total sorption; I. A., irreversible adsorption; R. A., reversible adsorption. Ni VII: Curve 1, T. S.; Curve 2, I. A.; Curve 3, R. A. Each remaining curve, 4–11, involves successive sorption without intermediate removal of strongly sorbed oxygen. Ni VII: Curve 4, T. S. Ni VI: Curve 5, T. S.; Curve 6 (equilibrium) T. S.; Curve 7, I. A.; Curve 8, R. A. Ni VI (sintered): Curve 9, T. S.; Curve 10, I. A.; Curve 11, R. A.

Comparing Curves 1 and 4 in Fig. 3, for total sorption on Ni VII, since they represent the usual, and the unusual, method (already mentioned) of obtaining isobars, it is apparent that the procedure used in obtaining Curve 4 has resulted in an increased total sorption of 9.8 cc. at 0°, which when corrected for the 2.5 cc. of slow sorption which occurred at the lower temperatures gives a net increase of 7.3 cc. to be accounted for. Similar instances of this effect were also exhibited by Ni VI. In an endeavor to learn more about the effect of temperature sequence upon sorption, Ni VII was evacuated after the completion of Isobar 4 and sorption again started at −190°. The initial reversible adsorption of 20 cc. was again found, also an irreversible adsorption of 8.6 cc. which, however, was immediately desorbed upon heating to 0°. This experiment indicates that the oxygen first sorbed at −190° underwent a change in configuration upon heating to 0° and an unsaturation of surface was created, even though the irreversible adsorption had increased over 40% while at −78 and 0°. In another instance, the sorption measurements begun at 24°, on a freshly reduced surface of Ni VII, to determine the last point on Curve 1, Fig. 3, were continued at −190°, after evacuating the catalyst, and an increase of 12.55 cc. irreversible adsorption was found. This amount was immediately desorbed upon raising the temperature back to 24°. Since an extrapolation of Curve 4 to 24° would cause it to lie some 12 to 13 cc. above Curve 1, it seems very probable that had sorption been started at −190° this increment would not have been wholly desorbed but would have appeared in part as enhanced sorption. At all events it is clear that enhanced sorption such as was obtained at 0° by starting at −190°, was not obtained when sorption at −190° took place on a surface previously saturated at 24°.

Discussion

The peculiarities which differentiate the observed sorptive behavior of oxygen from that of a gas like hydrogen on catalytically active metals for example are mainly the former's large zero pressure adsorption, and the impossibility of removing such adsorption even at high temperatures, which, incidentally, necessitated the somewhat unusual experimental method of attack. It has been found that the magnitude and the type of oxygen sorption depend not only upon the activity and temperature of the nickel surface, but also upon the temperature sequence followed. The rate curves, and, except for the peculiarities above noted, the isotherms and isobars for oxygen, are not abnormal. Because of the ease with which the large irreversible oxygen adsorption found at all temperatures could be completely removed with hydrogen, *i. e.*, below 100° if not first heated to convert it to oxide, it is believed that true oxide formation does not have any considerable part here. Neither is dissolved oxygen indicated because at 0° and above where solution should have become more marked, it was increasingly easy to pump off reversibly adsorbed oxygen which in no case involved gas taken up by slow sorption. Since the irreversible adsorption has the characteristics of activated adsorption[5] one must assume that the latter can occur instantaneously, at least on the most active portions of the nickel even at −190°, its rate finally falling to a value which is greater the higher the temperature. The reversible adsorption at −190° must be largely capillary condensation and, at higher temperatures, molecular adsorption. The evidence already presented indicating that oxygen sorbed at a lower temperature is transformed to a different type of sorption complex at a higher temperature, namely, the desorption of oxygen irreversibly held on the less active surfaces by heating, and its readsorption; the unsaturation at −190° produced by heating to 0° a surface already saturated at −190°, may well demand the presence of more than one type of activated adsorption as would also the enhanced sorption obtained at 0° by starting sorption at −190°.

(5) Taylor, THIS JOURNAL, **53**, 578 (1931); Taylor and Williamson, *ibid.*, **53**, 2168 (1931); Taylor, *Chem. Rev.*, **9**, 29 (1931); Taylor and Sickman, THIS JOURNAL, **54**, 602 (1932); Taylor, *Trans. Faraday Soc.*, **28**, 131 (1932); Taylor and Sherman, *ibid.*, **28**, 247 (1932); Benton and White, THIS JOURNAL, **54**, 1373 (1932).

Summary

1. Large amounts of oxygen have been found to be instantaneously and irreversibly adsorbed by catalytically active nickel even at −190°. The amount of such low temperature sorption is greater the more active the surface. In general the amount of irreversible adsorption increases with the temperature.

2. Large amounts of reversibly adsorbed oxygen occur only at −190°.

3. Sintered and regenerated nickel surfaces possess certain like and different sorptive characteristics.

4. The rates of slow sorption are small at −190°, but increase with the temperature, and at a given temperature are greater the more active the surface.

5. The interpretation of the various phenomena observed makes it most probable that activated adsorption occurs even at −190° and is the major fraction of the oxygen sorbed at 0°.

PROVIDENCE, R. I.

RECEIVED JUNE 30, 1933
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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE CARNEGIE INSTITUTE OF TECHNOLOGY AND THE CARNEGIE HIGH SCHOOL]

The Ternary System Diphenyl–Diphenylamine–Benzophenone

BY H. HOWARD LEE AND J. C. WARNER

Diagrams for the binary systems of diphenyl, diphenylamine and benzophenone were reported in a previous paper.[1] In the present investigation the freezing point–composition diagram for the *ternary* system of these components has been determined. The method of purification and the experimental procedure have been the same as in the previous investigation.

With most samples the initial crystallization temperature was checked by determining the temperature at which the solid phase disappeared. To accomplish this, a large number of solidified samples were placed in a thermostat set at a suitable temperature. After a period of from eight to ten hours, a record was made of samples which were completely liquid at the thermostat temperature. The temperature of the thermostat was then increased by from 0.1 to 1.0° depending upon the appearance of the remaining samples. After eight to ten hours, another record was made. The samples were freshly solidified each time the temperature of the thermostat was changed. This procedure for determining the temperature at which the solid phase disappeared was referred to as "thermostating" in a previous paper.[1]

Experimental Results.—The distribution of the samples used is indicated by the circles in Fig. 1. The experimentally determined initial crystallization temperatures, final solidification temperatures and temperatures for disappearance of solid are listed in Table I. The conventional ternary model, Fig. 2, was constructed from the data in Table I by inserting small steel rods of proper lengths to indicate temperatures in holes in a triangular wooden base representing compositions. The tops of the rods were pointed and the model was filled in with plaster of Paris to the tips of the rods. The intersections of the surfaces of the solid model are indicated by the boundary lines in Fig. 1. The intersections of these lines indicated approximately the eutectic compositions. A number of additional samples (not shown in Fig. 1) were then made up to determine more definitely the two ternary eutectic compositions and temperatures.

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[1] Lee and Warner, THIS JOURNAL, 55, 209 (1933).

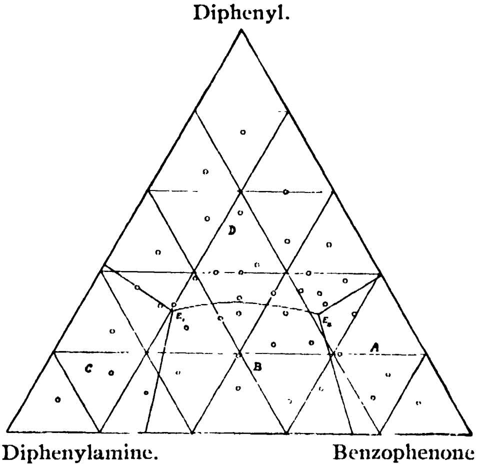

Fig. 1.

The ternary eutectic compositions (E_1 and E_2) are given in Table I. The average of seven final solidification temperatures yields a temperature of 18.8° for E_1. An average of eight final solidification temperatures gives 16.5° for E_2. From the solid figure and the data in Table I, the contours for the liquidus surfaces were plotted in Fig. 3.

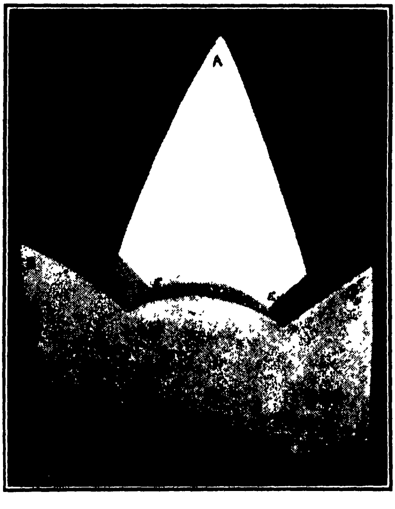

Fig. 2.—A, Diphenyl, m. p. 69.0°; B, diphenylamine, m. p. 52.8°; C, benzophenone, m. p. 47.7°; E_1 and E_2 are the ternary eutectics.

In the investigation of the system diphenylamine–benzophenone,[1] it was found that the compound between the components existed in two forms; a stable form with a melting point of 40.2° and a metastable form melting at 30.8°. The existence of the metastable compound would lead one to predict two metastable ternary eutectics. We have been able to verify this prediction experimentally and have determined approximately the metastable eutectic compositions and temperatures from cooling curves on freshly prepared samples, crystallized without inoculation, and the projection of the surfaces of the solid figure. Metastable E$_1'$ has the approximate composition 28 mole per cent. diphenyl, 47 mole per cent. diphenylamine and 25 mole per cent. benzophenone. The approximate eutectic temperature for E$_1'$, as determined from the average final solidification temperatures of seven samples, is 15.0°. The composition of E$_2'$ is approximately 28.5 mole per cent. diphenyl, 20.5 mole per cent. diphenylamine and 51.0 mole per cent. benzophenone. From the average final solidification temperatures of four samples, the eutectic temperature for E$_2'$ is 13.1°.

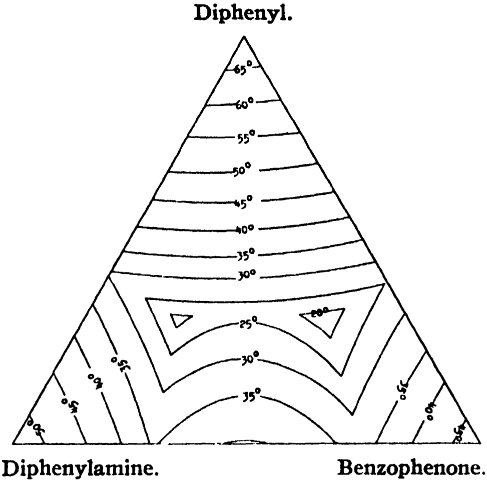

Fig. 3.

TABLE I

Region Fig. 1	Mole % $(C_6H_5)_2$	Mole % $(C_6H_5)_2NH$	Mole % $(C_6H_5)_2CO$	Init. cryst., °C.	Final solidification, °C.	Disapp. of solid, °C.
A	8.0	7.0	85.0			40.3
	9.2	16.2	74.6	31.2		31.6
	15.0	10.0	75.0	34.1		34.3
	20.0	18.0	62.0			24.3
	30.0	10.0	60.0	23.8		24.1
B	8.0	35.0	57.0	34.3		34.9
	11.5	26.1	62.4	30.0		30.3
	11.2	44.4	44.4	34.4		35.2
	15.0	55.4	29.6	30.2		30.8
	19.7	40.15	40.15			31.8
	22.2	31.0	46.8	28.0		29.0
	22.5	22.9	54.6			25.0
	26.1	48.2	25.7			24.9
	28.6	39.9	31.5	22.6	18.7	24.1
	30.0	35.0	35.0	25.5		25.7
	30.0	25.0	45.0	21.3	16.5	23.3
E$_2$	30.0	18.0	52.0	16.6	16.5	16.7
C	8.0	85.0	7.0			45.4
	10.0	65.0	25.0	31.2		31.5
	15.0	70.0	15.0	35.8		36.0
	25.0	65.0	10.0	32.8		33.4
	31.5	51.3	17.2	22.0	19.0	22.0
	36.0	54.0	10.0			25.7
E$_1$	30.5	49.0	20.5	18.8	18.8	19.0

TABLE I (*Concluded*)

Region Fig. 1	Mole % $(C_6H_5)_2$	Mole % $(C_6H_5)_2NH$	Mole % $(C_6H_5)_2CO$	Init. cryst., °C.	Final solidification, °C.	Disapp. of solid, °C.
	31.3	49.5	19.2	19.2	18.8	20.0
	31.1	48.8	20.1	19.0	18.7	19.6
	33.8	33.1	33.1			24.8
	35.0	25.0	40.0	23.3		23.9
	32.25	15.15	52.6	18.8	16.6	19.3
	30.9	16.7	52.4	17.2	16.5	17.8
	30.9	17.2	51.9	16.8	16.5	17.6
	35.0	15.0	50.0		16.6	22.7
	35.8	18.95	45.25			24.2
	38.0	8.0	54.0	24.6	16.5	25.1
	38.3	40.1	21.5	22.7	19.0	23.8
D	40.0	35.0	25.0	28.9	18.7	29.4
	40.0	30.0	30.0			29.4
	40.0	15.0	45.0	28.1	16.5	28.3
	42.0	25.0	33.0	30.5		30.7
	45.0	45.0	10.0	33.3		33.7
	47.0	7.0	46.0	34.0		34.2
	48.6	15.2	36.2	36.2		36.5
	53.8	30.1	16.1	40.9		41.4
	55.0	22.5	22.5			42.0
	60.0	10.0	30.0	43.8		44.2
	65.0	25.0	10.0	48.9		
	75.0	12.0	13.0	55.1		

Summary

The freezing point–composition diagram for the ternary system diphenyl–diphenylamine–benzophenone shows two stable ternary eutectics. One eutectic (E_1) has the composition 30.5 mole per cent. diphenyl and 49.0 mole per cent. diphenylamine. This eutectic temperature is 18.8°. The other eutectic (E_2) occurs at 30.0 mole per cent. diphenyl and 52.0 mole per cent. benzophenone, and at 16.5°.

Evidence is presented for the existence of two metastable ternary eutectics.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Rotation of Polar Groups in Organic Compounds

BY JULIAN M. STURTEVANT

The problem of the intramolecular rotation of polar groups in organic compounds about a single bond was first attacked theoretically by Williams[1] on the assumption that such rotation is perfectly free. He obtained for the average electric moment of a molecule containing two similar polar groups rotating about a common axis the relation

$$\bar{\mu} = \sqrt{2}m \sin \vartheta \tag{1}$$

where m is the magnitude of the group moments and ϑ is the angle the moments make with the axis of rotation. To make this equation fit the experimental values for the ethylene dihalides, $X{\cdot}CH_2{\cdot}CH_2{\cdot}X$, it was necessary to assume considerable distortion of ϑ from the normal value for the tetrahedral carbon atom. This distortion was attributed to the repulsive forces between the polar groups.

It is more reasonable to suppose that any repulsive forces would result in a more or less pronounced restriction of the rotation of the groups. Meyer[2] treated the problem from this point of view. By taking into account the mutual potential energy of the group dipoles, he showed that on the classical theory the right member of equation (1) should be multiplied by the factor $(1 - X)$, where

$$X = \frac{\alpha/(kT) + \beta/(kT)^2 + \gamma/(kT)^3 + \dots}{m + n/(kT) + o/(kT)^2 + p/(kT)^3 + \dots} \tag{2}$$

In this equation, k is the Boltzmann constant, T is the absolute temperature and the coefficients are determined by the dimensions of the molecule. As pointed out by Greene and Williams,[3] this result means that to a second approximation the plot of molar polarization against the reciprocal of the absolute temperature should be a parabola rather than the straight line required by the theory of Debye[4] for molecules having a constant dipole moment. These authors and Zahn[5] have found that the results of measurements on the ethylene dihalides and on diacetyl, $CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$, in the vapor state are in agreement with this prediction.

Zahn and others[6] have suggested that in some cases, at least, it may be necessary to quantize the intramolecular rotation of polar groups. This should be particularly true with molecules in which the dipole interactions are comparatively large. Smyth, Dornte and Wilson[7] have investigated this quantization in the case of ethylene dichloride, and have shown that the energy levels are so close together that the quantum treatment should not constitute a significant improvement over Meyer's classical analysis. The method they followed would have involved the use of the so-called Mathieu functions in the actual calculation of the electric moment. The theory of these functions is in such a state of development that such calculations, carried to temperatures as high as 300°K., would necessitate an amount of tedious labor out of all proportion to the accuracy of the original assumptions or the results that might be obtained. It will be shown in the present paper that a simple change in the form of the potential energy function used avoids the introduction of the troublesome Mathieu functions, the easily handled Hermite functions entering in their place. The results obtained are entirely in accord with experimental observations and with the qualitative predictions of Smyth, Dornte and Wilson. The present calculations have been carried out for diacetyl rather than for ethylene dichloride, since the smaller moments of inertia of the rotating groups should lead to greater deviations from the classical theory.

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(1) Williams, *Z. physik. Chem.*, **A138**, 75 (1928).

(2) Meyer, *ibid.*, **B8**, 27 (1930).

(3) Greene and Williams, *Phys. Rev.*, **42**, 119 (1932).

(4) Debye, "Polar Molecules," Chemical Catalog Company, Inc., New York, 1929, p. 37.

(5) Zahn, *Phys. Rev.*, **38**, 521 (1931); **40**, 291 (1932).

(6) *Cf.* Eyring, *ibid.*, **39**, 746 (1932).

(7) Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

Electric Moments.—Suppose m_1, m_2, represent the components of the rotating group moments perpendicular to the common axis of rotation, m_3 the sum of the components of all the group moments parallel to the axis, and φ the angle between m_1 and m_2. The square of the resultant moment of the molecule is given by

$$m^2 = m_1^2 + m_2^2 + m_3^2 + 2m_1m_2 \cos \varphi \tag{3}$$

The mean square moment of the molecules having intramolecular rotational energy ϵ_i is then

$$\bar{\mu}_i^2 = \int_0^{2\pi} m^2\psi_i^2 d\varphi \tag{4}$$

ψ_i is the normalized wave function corresponding to this energy level. It is assumed that the other modes of motion of the molecules or the groups within them have no appreciable effect on the rotation of the polar groups, or on the magnitudes or positions of the group dipoles. The mean square moment at any temperature is

$$\bar{\mu}^2 = \Sigma p_i \bar{\mu}_i^2 \, e^{-\Delta\epsilon_i/kT} / \Sigma p_i \, e^{-\Delta\epsilon_i/kT} \tag{5}$$

where $\Delta\epsilon_i = \epsilon_i - \epsilon_0$ and p_i is the quantum weight of the i^{th} state.

Potential Energy Function.—Following Smallwood and Herzfeld[8] and Smallwood,[9] the individual group moments have been assumed to lie along the valence bonds and to be located at the circumferences of the atoms involved. These assumptions differ somewhat from the model used by Meyer. Smyth, Dornte and Wilson have shown that the two methods of locating the group moments lead to values of the potential which are in qualitative agreement with each other in the case of ethylene dichloride.

Two dipoles, $m_1 = q_1d_1$, $m_2 = q_2d_2$, separated from each other by a

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(8) Smallwood and Herzfeld, THIS JOURNAL, 52, 1919 (1930).

(9) Smallwood, *ibid.*, 54, 3048 (1932).

distance D large compared to d_1 and d_2 have a mutual potential energy given by

$$V = (-m_1m_2/D^3)(2 \cos \eta_1 \cos \eta_2 - \sin \eta_1 \sin \eta_2 \cos \chi) \tag{6}$$

Here η_1, η_2 are the angles between the dipoles and the line joining them, and χ is the angle between their projections in a plane perpendicular to this line. These quantities may be expressed as functions of the angle φ of equation (3); expansion of the resulting expression for V about the position of minimum potential energy, φ_0, gives

$$V = a_0 + a_2(\varphi - \varphi_0)^2 + a_4(\varphi - \varphi_0)^4 + \ldots \tag{7}$$

where the coefficients are rather complicated functions of the molecular dimensions, etc. Their values for diacetyl and formic acid, HCOOH, are given in Table I; in each case the interactions included in the calculations and the value of φ_0 are indicated. The molecular dimensions and group moments used were those given by Smallwood.[9] Polarization effects were neglected. Smyth, Dornte and Wilson expanded the potential function for ethylene dichloride in a Fourier series, and in their calculations neglected the terms after the first two. The Fourier expansion for diacetyl is as follows

TABLE I

COEFFICIENTS (ERGS × 10^{14}) IN THE EXPANSION OF THE POTENTIAL ENERGY FUNCTION

Substance	a_0	a_2	a_4	a_6	Interactions included	φ_0
Diacetyl	17.7	7.17	−1.23	0.25	C:O—C:O; C:O—C·H; C·H—C·H	π
Formic acid	−40.7	9.19	−2.33	0.49	C:O—O·H; C·H—O·H	0

$$V = (30.82 + 13.11 \cos \varphi + 0.28 \cos 2\varphi + 0.27 \cos 3\varphi + \ldots) \times 10^{-14}$$

Wave Equation.—The wave equation for the intramolecular rotation is separable by well-known methods. The equation involving the variable φ is found to be

$$\frac{d^2\psi}{d(\varphi - \varphi_0)^2} + \frac{8\pi^2 I}{h^2} [\epsilon - \Sigma a_{2j} (\varphi - \varphi_0)^{2j}] \psi = 0 \tag{8}$$

I is the reduced moment of inertia, $I_1I_2/(I_1 + I_2)$, and $I_i = M_ir_i^2 \sin^2 \vartheta_i$, where M_i is the mass of the i^{th} rotating group, ϑ_i is the angle between the valence bond to this group and the axis of rotation, and r_i is the distance along the valence bond from the axis to the center of mass of the group. (The group is assumed to be symmetrical about the extension of the valence bond.)

In general, equation (8) has to be treated by approximate methods. For example, if the terms in the potential function for which $j > 1$ are small enough, they may be taken as perturbation terms, so that the wave equation for the unperturbed system is simply that of the torsional harmonic oscillator. If the interaction is sufficiently strong, the wave functions and energy values may be identified with those of the linear oscillator, since neglect of the actual system's periodic nature involves no appreciable error. The first approximation to the true proper functions and values may then be obtained by Schrödinger's method for non-degenerate systems.

Diacetyl.—Zahn[10] has made a careful experimental study of the temperature variation of the electric moment of diacetyl. He found the average value of $(\varphi - \varphi_0)$ to be about 30–40° at moderate temperatures. Calculation shows that even at 600°K. an average error of only 8% will be introduced into the variable part of the potential by neglecting the terms in $(\varphi - \varphi_0)^4$ and $(\varphi - \varphi_0)^6$, and the resulting expression agrees on the average to within 3% with the potential taken in the form $V = c_0 + c_1 \cos \varphi$, the form used by Smyth, Dornte and Wilson in their calculations with ethylene dichloride. To this approximation the wave functions are $\psi_n = (1/N_n)e^{-s^2/2}H_n(s)$, $n = 0, 1, 2, \ldots$, where N_n is the normalizing factor, H_n is the n^{th} Hermitian polynomial, and the variable s is defined by the relations $s = (\varphi - \pi)/a$ and $a^2 = h/2\pi \sqrt{1/2Ia_2}$. The functions ψ_n may be normalized in the same manner as for the linear harmonic oscillator since any contributions to the integrals $\int_{-\infty}^{+\infty} e^{-s^2} H_n^2(s)\, ds$ corresponding to values of $(\varphi - \pi)$ for which $|\varphi - \pi| > \pi$ are negligible (for diacetyl, $s \approx 5(\varphi - \pi)$). The value of N_n is then $\pi^{1/4}\, 2^{n/2}\, (n!)^{1/2}$. The energy levels corresponding to these wave functions are $\epsilon_n = a^2a_2(2n + 1) + a_0$.

In the variable s, equation (3) for a symmetrical molecule with $m_1 = m_2$ and $m_3 = 0$ becomes

$$m^2 = m_1^2\left(a^2s^2 - \frac{a^4s^4}{12} + \frac{a^6s^6}{360} - \ldots\right) \tag{9}$$

The integrals involved in the calculation of $\bar{\mu}_i^2$ by equation (4) can be expressed very simply as follows

$$\int_{-\infty}^{+\infty} s^2\, \psi_i^2\, ds = {}^1/_2(2i + 1)$$

$$\int_{-\infty}^{+\infty} s^4\, \psi_i^2\, ds = {}^3/_4\,(2i^2 + 2i + 1)$$

$$\int_{-\infty}^{+\infty} s^6\, \psi_i^2\, ds = {}^{15}/_8\,({}^4/_3 i^3 + 2i^2 + {}^8/_3 i + 1)$$

Using these relations we obtain $\bar{\mu}_i^2$ as a power series in i.

Since the constant a^2 is small, the energy levels are close together, and it is therefore permissible at temperatures not too low to calculate $\bar{\mu}^2$ by replacing the summations in equation (5) by integrals. This is most conveniently accomplished by noting that $i^n\, e^{-\beta i} \approx \int_{i-1/2}^{i+1/2} x^n\, e^{-\beta x}\, dx$, so that

$$\sum_{i=0}^{\infty} i^n\, e^{-\beta i} \approx \int_{-1/2}^{\infty} x^n\, e^{-\beta x}\, dx = \frac{(-1)^n\, e^{\beta/2}}{\beta}\left[\frac{1}{2^n} - \frac{n}{\beta 2^{n-1}} + \frac{n(n-1)}{\beta^2\, 2^{n-2}} - \ldots + (-1)^n \frac{n!}{\beta^n}\right]$$

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(10) Zahn. *Phys. Rev.*, **40**, 291 (1932).

In this way it is readily found, since $p_i = 1$ in the present case, that

$$\bar{\mu}^2 \approx m_1^2 \left[-\frac{a^4}{32} + \left(1 + \frac{5a^4}{576}\right)\frac{kT}{2a_2} - \frac{(kT)^2}{16a_2^2} + \frac{(kT)^3}{192a_2^3} - \ldots \right] \tag{10}$$

The accuracy of this method of approximation was tested by numerical calculation for the rather unfavorable case for which $a_2 = 10^{-13}$ and $a^2 = 0.2$. It was found that the value of $\bar{\mu}$ at 200°K. calculated by equation (10) was only 1.5% lower than that obtained by direct evaluation of the summations in equation (5).

It is of interest to compare equation (10) with the results obtainable on the classical theory of Meyer. In cases where the dipole interaction is large, Meyer's method of calculation leading to equation (2) is very tedious because of the slow convergence of the expansion of $e^{-V/(kT)}$. However, when it is possible to write $V = a_0 + a_2(\varphi - \varphi_0)^2$, the calculations can be performed very simply in a different way. For diacetyl the mean square moment is given by

$$\bar{\mu}^2 = \frac{\int m^2 e^{-V/(kT)}\, d\vartheta}{\int e^{-V/(kT)}\, d\vartheta} = 2m_1^2 \left[1 - \frac{\int_{-\infty}^{+\infty} \cos\vartheta\, e^{-a_2\vartheta^2/(kT)}\, d\vartheta}{\int_{-\infty}^{+\infty} e^{-a_2\vartheta^2/(kT)}\, d\vartheta} \right]$$

where $\vartheta = \varphi - \pi$. No appreciable error is made in taking the limits of integration as $-\infty$ and $+\infty$ instead of $-\pi$ and $+\pi$, and the evaluation of the integrals is rendered very much easier. We thus obtain the expression

$$\bar{\mu}^2 = 2m_1^2\,[1 - e^{-kT/(4a_2)}] \tag{11}$$

To compare this with equation (10) we expand the exponential

$$\bar{\mu}^2 = m_1^2 \left[\frac{kT}{2a_2} - \frac{(kT)^2}{16a_2^2} + \frac{(kT)^3}{192a_2^3} - \ldots \right] \tag{12}$$

The error caused by neglecting higher terms is about 5% or less at 300°K. The value of a^4 for diacetyl is approximately 0.002, so that equations (10) and (12) are practically identical for this molecule.

It is probable that similar agreement between the classical and wave-mechanical results at temperatures in the neighborhood of 300°K. would be obtained with molecules whose dipole interactions can only be given by expressions containing powers of $(\varphi - \varphi_0)$ up through the fourth or sixth. The treatment in such cases would obviously be very much more difficult. Calculations have been carried through for molecules having comparatively small interactions, such as hydroquinone, p-$C_6H_4(OH)_2$, and terephthalic aldehyde, p-$C_6H_4(CHO)_2$, and the results at temperatures above 200°K. differ in no respect from those obtained on the classical theory. The former substance was treated by perturbation methods, taking as zero order approximation the rotator with one degree of freedom. The potential function for terephthalic aldehyde was taken in the form $V =$

$c_0 + c_1 \cos \varphi$, so that the proper functions were constant multiples of the Mathieu functions of even order.[11,12]

The values of the root mean square moment of diacetyl calculated by equation (11) are plotted against the temperature in Fig. 1, along with the values determined experimentally by Zahn.[10,13] The excellent agreement between the calculated and observed values is to be considered as fortuitous in view of the uncertain nature of the molecular model used, the approximations made in the calculations and the complete neglect of polarization effects, which latter might be expected to be rather important because of the close approach of a carbonyl group to the hydrogens on the methyl group attached to the other central carbon atom at the position of minimum potential.

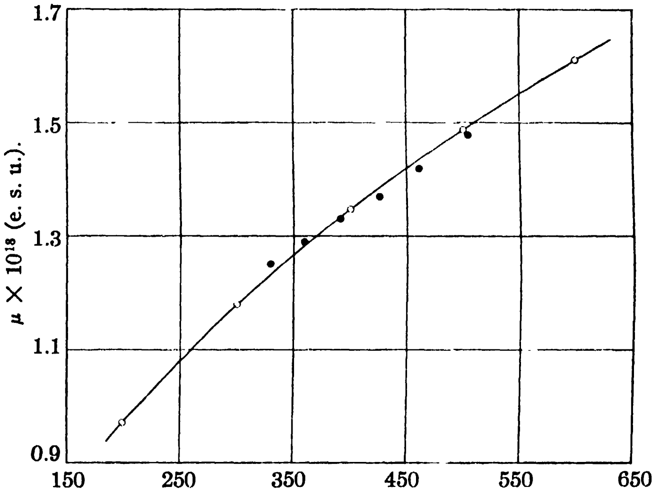

Fig. 1.—Electric moment of diacetyl: ○, calculated by equation (11); ●, observed by Zahn, Ref. 10, p. 293.

Formic Acid.—The term involving $(\varphi - \varphi_0)^4$ in the potential function for formic acid is rather large to be neglected, so that the above treatment was not employed. The resultant moment for this molecule was calculated on the classical theory, using Simpson's rule for the evaluation[14] of the

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(11) *Cf.* Whittaker and Watson, "Modern Analysis," Fourth ed., University Press, Cambridge, 1927, p. 404; Goldstein, *Trans. Cambr. Phil. Soc.*, **23**, 303 (1927); Condon, *Phys. Rev.*, **31**, 891 (1928).

(12) In this case the calculations involving the Mathieu functions were very much easier than they would be with diacetyl or ethylene dichloride since the value of the parameter q occurring in Mathieu's equation

$$(d^2\psi/dx^2) + (4\alpha - 16q\cos 2x)\psi = 0 \quad (x = {}^1/_2\varphi)$$

had the comparatively small value 8.05.

(13) These values reported by Zahn were not calculated by the method recommended by Greene and Williams, Ref. 3. However, this change would make no appreciable difference in the agreement between experiment and theory.

(14) These calculations were facilitated by the convenient table of values of e^{-x^2} given by Newman, *Trans. Cambr. Phil. Soc.*, **13**, 145–241 (1883).

integrals involved. The mean square moment is given by the relation

$$\bar{\mu}^2 = m_1^2 + m_2^2 + m_3^2 + 2m_1m_2 \frac{\int_0^{2\pi} \cos\varphi \, e^{-V/(kT)} \, d\varphi}{\int_0^{2\pi} e^{-V/(kT)} \, d\varphi} \qquad (13)$$

The values of $\bar{\mu}^2$ calculated by this equation are listed in Table II. They fall on the curve

$$\bar{\mu}^2 \times 10^{36} = 1.370 + 3.62 \times 10^{-3}T + 2.9 \times 10^{-8}T^2 - 1.7 \times 10^{-9}T^3 \qquad (14)$$

TABLE II

ELECTRIC MOMENT OF FORMIC ACID CALCULATED BY EQUATION (13)

T, °K	200	300	400	500
$\bar{\mu}^2 \times 10^{36}$ (e. s. u.)	2.08	2.41	2.71	2.98
$\bar{\mu} \times 10^{18}$ (e. s. u.)	1.44	1.55	1.65	1.73

Equation (11) leads to values of $\bar{\mu}$ which range from 3 to 6% lower than those given in Table II.

Meyer[15] arrived at the conclusion that the carboxyl group should show no change of electric moment with temperature in the neighborhood of 300°K. However, he only carried his calculations through a first approximation, which, as he pointed out in discussing ethylene dichloride, is not sufficient in cases where the dipole interactions are large. He then compared the lower limit for the moment calculated in this way with the experimental values for formic[16] and benzoic[17] acids then available. The close agreement led him to believe that rotation is completely frozen out at ordinary temperatures. Zahn[18] has made a careful study of the temperature variation of the dielectric constant of formic acid vapor. He found that the apparent electric moment increases with the temperature, but he was able to account for the observed molecular polarizations by consideration of the partial association of formic acid into double molecules, with the assumption that the single and double molecules have *constant* moments equal to 1.51 and 0.99 $\times$ 10^{-18}, respectively. He used the equations given by Coolidge[19] to calculate the degree of association, and assumed that the constant part of the polarization is doubled on association.

The results in Table II indicate that the assumption of a constant moment for the single molecules is questionable. If one uses for $\bar{\mu}^2$ for the single molecules the values given by equation (14), and assumes a moment equal to zero for the double molecules, one obtains the molecular polarization in the form

$$P = (n_1 + 2n_2)A + n_1(\beta_0/T + \beta_1 + \beta_2T + \beta_3T^2) \qquad (15)$$

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(15) Meyer, Ref. 2, p. 37.

(16) Wolf, *Physik. Z.*, **31**, 227 (1930).

(17) Williams, *ibid.*, **29**, 174 (1928).

(18) Zahn, *Phys. Rev.*, **37**, 1516 (1931).

(19) Coolidge, THIS JOURNAL, **50**, 2166 (1928).

where n_1, n_2 are the mole fractions of the single and double molecules, respectively. Zahn used the value 8.53 for A. The values of P calculated in this way are given in the second line of Table III. The experimental values of Zahn are listed in the third line.

TABLE III

MOLECULAR POLARIZATION OF FORMIC ACID

T, °K	344.6	386.9	403.1	423.4
Calcd. by eq. (15) P, cc.	32.69	41.86	44.59	46.14
Observed	41.43	41.40	41.34	41.26

The trend of the calculated values indicates that the assumption of a zero moment for the double molecules is erroneous. The theoretical curve could be made to parallel the experimental curve by assuming a finite moment for the double molecules which *decreases* with increasing temperature. This would be the result of a gradual loosening of the forces holding the two formic acid units away from the anti-parallel position. However, attempts at a quantitative treatment of this effect would not be worth while because of the very limited information concerning the associated molecules.

In conclusion, the author wishes to express his appreciation of the very helpful discussions he has had with Prof. Henry Margenau of the Department of Physics during the course of this work.

Summary

1. In certain cases of strong dipole interaction between polar groups capable of rotation about a single bond in organic molecules, application of quantum methods to the study of the motion of these groups leads to practically the same results as those obtained on the classical theory at temperatures within the range of experimental observations. In one such case, diacetyl, the calculated values of the electric moment agree very well with experiment over a temperature range of 200°.

2. Classical calculations indicate that the electric moment of formic acid should show a considerable temperature variation, which is not in disagreement with experimental observations.

NEW HAVEN, CONN.

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[Contribution from the Department of Chemistry, Cornell University]

Germanium. XL. Action of Ammonia upon Monochloromonogermane and Dichloromonogermane. Action of Water upon Monochloromonogermane[1]

By L. M. Dennis and R. W. Work

Introduction.—The action of anhydrous ammonia upon the mono-, di-, and trihalogen derivatives of methane and monosilane has been studied by various investigators. They may briefly be summarized as follows

$$4CH_3I + 4NH_3 = N(CH_3)_4I + 3NH_4I^2$$
$$6CH_2Cl_2 + 16NH_3 = (CH_2)_6N_4 + 12NH_4Cl^3$$

$CHCl_3$ (in sealed tube with ammonia and absolute alcohol).—Chief product NH_4CN.[4]

$SiH_3Cl + NH_3$.—Stock and Somieski found[5] that, with excess of ammonia, the compound at once lost all of its chlorine to form ammonium chloride, and that the silicon retained its three atoms of hydrogen, forming nitrogen-containing derivatives of monosilane such as the volatile $(SiH_3)_2NH$.

They give the reaction of dichloromonosilane with excess of ammonia as $SiH_2Cl_2 + 3NH_3 = SiH_2(NH) + 2NH_4Cl$, the silicon compound forming at once a solid, non-volatile polymer.

With excess of ammonia, $SiHCl_3$ forms[6] $(SiH{\cdot}NH)_2NH$.

No halogenated derivatives of the normal hydrides of tin and lead are as yet known, but since such compounds of germanium are available,[7] the study of their behavior when treated with an excess of ammonia, with a view to ascertaining to what extent the reactions were analogous to those of the corresponding compounds of carbon and silicon, was taken up.

Experimental

Monochloromonogermane, GeH_3Cl, and dichloromonogermane, GeH_2Cl_2, were prepared from pure monogermane by the method of Dennis and Judy.[7] The purity was checked by determinations of molecular weight. Calcd. for GeH_3Cl, 111.1; found, 110.8, 109.9. Calcd. for GeH_2Cl_2, 145.5; found, 145.6.

Reaction of Monochloromonogermane with Ammonia.—The experiments were carried out in the vacuum fractionation apparatus, as modified by Laubengayer and Corey,[8] but all of the bulbs were provided with stopcocks and normal, interchangeable, ground joints, which made it possible to disconnect them and attach them at any desired points on the apparatus.

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[1] This article is based upon the thesis presented to the Graduate School of Cornell University by Robert W. Work in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Chablay, *Ann. chim.*, [9] 1, 477 (1914).

[3] Höland, *Ann.*, **240**, 225 (1887).

[4] Heintz, *Ann. physik Chem.*, **174**, 263 (1856).

[5] Stock and Somieski, *Ber.*, **54**, 740 (1921).

[6] Stock and Zeidler, *ibid.*, **56**, 986 (1923).

[7] Dennis and Judy, This Journal, **51**, 2321 (1929).

[8] Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

A sample of GeH_3Cl was distilled into a weighed bulb on the apparatus, the stopcock of the bulb was closed, and the bulb was detached and weighed. The bulb was again attached, and ammonia was distilled upon the sample and was allowed to act for two hours at −78 to −50°. There appeared in the bulb a yellowish substance.

The bulb was held at −50° and the excess of ammonia was distilled into a second bulb by surrounding the latter with liquid air. The residue was now clearly seen to be a mixture of a white, crystalline compound and an amorphous powder. The first bulb was found to have lost weight, which showed that a volatile product had been removed with the ammonia. To ascertain its nature, the distillate in the second bulb was held at −78° and the ammonia was distilled over into a third bulb. Nothing remained in the second bulb. The distillate was then surrounded by a bath at −110° at which temperature ammonia has a vapor tension of only 1 mm.[9] Manometric readings disclosed the presence of a substance condensable with liquid air, but having an appreciable vapor tension at −135°. This was carefully distilled off at −135° and was further fractionally distilled to separate the gas from traces of ammonia and its volume was measured. Molecular weight, calcd. for GeH_4, 76.6; found, 76.2.

Ammonium chloride was undoubtedly formed in the reaction of the ammonia on the GeH_3Cl, and its amount in the reaction bulb was ascertained by utilizing the fact that it forms a triammonate, $NH_4Cl{\cdot}3NH_3$, for which the dissociation pressure–temperature curve is known. This indirect method of determining ammonium chloride was used by Pugh and Thomas,[10] who kept the pressure constant and varied the temperature of the bath. We departed from this procedure and kept the material at constant temperature, −5°, removing volumes of ammonia stepwise and thus lowering the decomposition pressure of the ammonate. The amount of ammonium chloride may be calculated from the volume of ammonia evolved between two points of equal pressure in the system before and after the $NH_4Cl{\cdot}3NH_3$ has been decomposed.

It having thus been ascertained that all of the chlorine in the GeH_3Cl is removed by the ammonia to form ammonium chloride, and that monogermane is simultaneously produced, there remained some hydrogen still to be accounted for. The presence of GeH_4 in the reaction products rendered it probable that an unsaturated hydride of germanium might first be formed and that this then dissociated with the production of GeH_4 and a lower hydride, thus

$$GeH_3Cl + NH_3 = NH_4Cl + GeH_2{}^{11}$$
$$3GeH_2 = GeH_4 + 2GeH$$

Germanium monohydride, $(GeH)_x$, was found by Dennis and Skow[12] to break down into metallic germanium and hydrogen when slightly heated. To learn whether the solid residue in the reaction bulb contained $(GeH)_x$, the bulb was touched with the flame of a Bunsen burner. There was instant formation of a black mirror on the wall of the bulb, and a rise of gas pressure in the apparatus. The gas, which was noncondensable by liquid air, was pumped off, measured and analyzed by combustion. It was found to be pure hydrogen.

The various data thus obtained indicate that the reaction proceeds according to the equation

$$3xGeH_3Cl + 3xNH_3 = 3xNH_4Cl + xGeH_4 + 2(GeH)_x \qquad (1)$$

and this is confirmed by the analytical results.

Anal. Sample of GeH_3Cl, 0.2342 g. NH_4Cl formed, calcd. 0.1128 g., found 0.1127 g.

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(9) Karwat, *Z. physik. Chem.*, **112**, 487 (1924).

(10) Pugh and Thomas, *J. Chem. Soc.*, 60 (1931).

(11) GeH_2 has recently been isolated by Royen and Schwarz, *Z. anorg. allgem. chem.*, **211**, 412 (1933).

(12) Dennis and Skow, THIS JOURNAL, **52**, 2369 (1930).

H_2 produced, calcd. for 2GeH, 0.001418 g., found, 0.001416 g. Sample of GeH_3Cl, 0.2831 g. GeH_4 formed, calcd., 0.0645 g., found, 0.0647 g.

The correctness of equation (1) is thus established.

Reaction of Monochloromonogermane with Water.—Upon treatment of monochloromonosilane with water, there is formed the volatile compound disiloxane,[13] b. p. −15.2°. $2SiH_3Cl + H_2O = (SiH_3)_2O + 2HCl$.

To ascertain whether an analogous compound of germanium is produced, water was distilled into a bulb containing GeH_3Cl. There was formed at once a white solid which gradually became light yellow in color. No evidence of the formation of a volatile compound of germanium was obtained.

Reaction of Dichloromonogermane with Ammonia.—Anhydrous ammonia was distilled in the fractionation chain upon a sample of GeH_2Cl_2 of known weight, the ammonia being first condensed by liquid air and then allowed to rise to −78°. At that temperature reaction took place at once, with the formation of a brown solid that became black in a few seconds. The bulb was allowed to come to room temperature and the excess of ammonia was then removed. No volatile substance other than ammonia was present. The reaction bulb was again weighed, and the weight of the ammonia that took part in the reaction was thus ascertained. Millimoles of NH_3, 4.682; of GeH_2Cl_2, 2.435. Ratio $NH_3:GeH_2Cl_2 = 1.997:1.000$.

The experiment was repeated with another sample, except that the reaction bulb was held at −27° and the ammonia was introduced very slowly. The reaction product was at first white, then changed to yellow and finally became black. The ratio $NH_3:GeH_2Cl_2$ was again determined and was found to be 2.067:1.000.

The residue in the reaction bulb was extracted with water, and crystals from the solution were identified as ammonium chloride under the microscope. The black powder was found to be insoluble in hydrochloric acid, both dilute and concentrated, in dilute sulfuric acid and in hydrofluoric acid. It was not attacked by 6 *N* sodium hydroxide, but when hydrogen peroxide was added, it quickly dissolved yielding a solution that contained germanium. These reactions identified it as free germanium.[14]

The experimental results show that when an excess of anhydrous ammonia acts upon dichloromonogermane, it does so in the ratio $2NH_3:GeH_2Cl_2$, that ammonium chloride is formed and germanium is simultaneously set free, and that no volatile substance is produced. The reaction is, therefore, $GeH_2Cl_2 + 2NH_3 = Ge + 2NH_4Cl$.

The elements in the fourth group show decreasing affinity for hydrogen with rise of atomic weight, methane being very stable, SiH_4 being decomposed into its elements at about 400°, GeH_4 at 285°, and the hydrides of tin and lead dissociating spontaneously.

The halogenated derivatives of methane react less readily with ammonia than do the analogous compounds of silicon and germanium, which may be explained by the fact that both the normal and maximum covalencies of carbon are four, and that it forms stable compounds with both hydrogen and the halogens.

If the next element in the group, silicon, is considered to have a maximum covalency of six,[15] then ammonia, with a lone pair of valency electrons, can act as a *donor*, and can form coördinate linkages with the silicon atom, with subsequent breakdown of the complex to form new molecules. The

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(13) Stock, Somieski and Wintgen, *Ber.*, **50**, 1754 (1917); Stock and Somieski, *ibid.*, **56**, 132 (1923).

(14) See Dennis, Tressler and Hance, THIS JOURNAL, **45**, 2033 (1923).

(15) Sidgwick, "The Electronic Theory of Valency," Oxford, 1927, p. 152.

investigations of Stock and his co-workers have shown that when the mono-, di-, and trichloro derivatives of monosilane are treated with ammonia, the affinity of the silicon for hydrogen is such that it retains, in the first reaction, all of the hydrogen atoms that it possessed before treatment with the ammonia, the chlorine being removed as a negative ion.

Germanium, standing below silicon in the group, has weaker affinity for hydrogen, and, when caused to react with ammonia, the chlorinated derivatives of monogermane, GeH_2Cl and GeH_2Cl_2, lose all of the halogen, and a part or all of the hydrogen.

The study, not as yet completed, of the action of ammonia upon trichloromonogermane indicates that there is first formed a diammonate, $GeHCl_3 \cdot 2NH_3$, and that this, upon further treatment with ammonia, is converted to germanous imide, GeNH.[16]

Summary

1. The reaction between monochloromonogermane and an excess of liquid ammonia is, $3xGeH_3Cl + 3xNH_3 = 3xNH_4Cl + xGeH_4 + 2(GeH)_x$.
2. The reaction between dichloromonogermane and an excess of liquid ammonia is $GeH_2Cl_2 + 2NH_3 = Ge + 2NH_4Cl$.
3. The reaction between monochloromonogermane and an excess of water produces neither hydrogen nor the hypothetical compound $(GeH_3)_2O$.

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[16] Johnson, Morey and Kott, THIS JOURNAL, 54, 4278 (1932).

ITHACA, NEW YORK

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The Thermodynamic Constants of Iodine Monochloride, Iodine Monobromide and Bromine Monochloride in Carbon Tetrachloride Solutions

BY CHARLES M. BLAIR, JR., AND DON M. YOST

Introduction

The changes in free energy, heat content and entropy of most reactions have been determined for only a single environment. In order to facilitate future studies on the relations between reactions taking place both in the gas phase and in solutions the determination of the thermodynamic constants of iodine monochloride, iodine monobromide and bromine monochloride in carbon tetrachloride was undertaken. The solvent, carbon tetrachloride, was chosen so that the resulting solutions would be as nearly perfect as possible. The constants for iodine monochloride,[1] iodine monobromide,[2] and bromine monochloride[3] have been previously determined for the case in which all substances are present as gases.

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[1] McMorris and Yost, THIS JOURNAL, 54, 2247 (1932).

In order to obtain the desired thermodynamic quantities, measurements were made on the partial vapor pressures of iodine monochloride and chlorine above their carbon tetrachloride solutions, on the heats of solution of iodine and bromine, and on the heats of formation of iodine monochloride, iodine monobromide and bromine monochloride when present in carbon tetrachloride solutions.

Experimental Method and Preparation of Materials

The vapor pressures of iodine monochloride and chlorine above their solutions in carbon tetrachloride were determined at 25° by a dynamic method, similar in most respects to that described by Bichowsky and Storch.[4] Dry nitrogen was forced from a rubber balloon through the solutions at a rate of about one liter per hour, and the volume delivered was determined by weighing the water used to deflate the balloon.[5] The iodine monochloride was absorbed in a sodium sulfite solution and the resulting iodide was determined by titration with standard permanganate solution according to the method described by Swift.[6] Preliminary experiments showed that no appreciable excess of either iodine or chlorine was present in the vapor. This was to be expected since iodine monochloride is only slightly dissociated (0.42%) at room temperature, and because a small excess (1%) of iodine was present in the solutions. In the experiments with chlorine the gas was absorbed in potassium iodide solution and the liberated iodine was titrated with standard thiosulfate.

The iodine monochloride solution was prepared by adding a small excess (1%) of iodine to a carbon tetrachloride solution of chlorine of known concentration. The small excess of iodine decreased the dissociation of the iodine monochloride without contributing appreciably to the total vapor pressure. All reagents were of the highest purity obtainable.

The calorimeter used consisted of a 1.5 liter Dewar flask equipped with an insulating cover, an electrically operated stirrer, a heating coil of platinum wire, and a Reichsanstalt Beckmann thermometer. The Dewar flask was surrounded by ample insulation and the whole enclosed in a wooden box.

In determining the heats of solution of iodine and bromine, weighed amounts of these substances were added to about one liter of carbon tetrachloride contained in the calorimeter. The halogens were contained in easily breakable glass bulbs attached to a glass rod passing through the cover. After the temperature rise of the calorimeter had become constant, the bulb was broken and the temperature change observed at regular intervals until the slow, steady rise resulting from the stirring again set in. In determining heats of reaction the carbon tetrachloride was replaced by a solution of chlorine or bromine in this solvent, and the concentrations were such that an excess was always present, thus making corrections for incomplete reaction unnecessary, except in the case of bromine monochloride. The heat capacity of the calorimeter was determined by passing a measured electric current through the heating coil for a known length of

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(2) McMorris and Yost, THIS JOURNAL, 53, 2625 (1931).

(3) The results, obtained by P. Murdoch, Philip Brass and Don M. Yost, have not yet been published, but are presented in the theses of the two former investigators. At room temperature a light absorption method was used (P. M.) and at higher temperatures advantage was taken of the reversible dissociation of nitrosyl chloride (P. B.) and phosgene (D. M. Y.).

(4) Bichowsky and Storch, THIS JOURNAL, 37, 2696 (1915).

(5) For further details see McMorris and Badger, *ibid.*, 55, 1952 (1933).

(6) Swift, *ibid.*, 52, 899 (1930).

time. The temperature changes accompanying solution or reaction varied from 0.120 to 0.300°.

Results of the Vapor Pressure Experiments.—In Table I are presented the results of the experiments on the partial vapor pressures at 25.0° of iodine monochloride above its solutions in carbon tetrachloride, together with the values for the constant of Henry's law $p_{\text{mm.}}/N_{\text{ICl}} = H_{\text{ICl}}$. The pressures, $p_{\text{mm.}}$, are given in millimeters and concentrations, N_{ICl}, in mole fractions.

TABLE I

PARTIAL PRESSURES OF IODINE MONOCHLORIDE ABOVE ITS CARBON TETRACHLORIDE SOLUTIONS AT 25.0°

Mole fraction of ICl, N_{ICl}	0.00159	0.00290	0.00496	0.00800	0 00933	0.0128	0.0203
Pressures of ICl in mm., $P_{\text{mm.}}$	.331	.594	1.05	1.70	1.94	2.68	4.16
$p_{\text{mm.}}/N_{\text{ICl}} = H_{\text{ICl}}$	208	209	212	212	209	209	205
H_{ICl} mean	209						

With the exception of the first two, all vapor pressures are the mean of several determinations. The concentrations cover a twelve-fold range while the values of H_{ICl} are practically constant with an average deviation from the mean of 1%. Henry's law is evidently obeyed quite closely. This was also found to be the case for iodine monobromide.[7]

Table II presents the partial pressures of chlorine above its carbon tetrachloride solutions at 25.0° together with the Henry's law constant, $p_{\text{mm.}}/N_{\text{Cl}_2} = H_{\text{Cl}_2}$.

TABLE II

PARTIAL PRESSURES OF CHLORINE ABOVE ITS CARBON TETRACHLORIDE SOLUTIONS AT 25.0°

Mole fraction of Cl_2, C_{Cl_2}	0.00394	0.00448	0.00609	0.00615	0.00690	0.00781	0.01245	0.01363	0.01391
Pressures of Cl_2 in mm., $p_{\text{mm.}}$	18.6	22.8	2.80	30.4	32.2	39.8	64.6	69.0	73.4
$p_{\text{mm.}}/N_{\text{Cl}_2} = H_{\text{Cl}_2}$	4730	5080	4600	4940	4670	5100	5180	5070	5280
H_{Cl_2} mean	4960								

The average deviation of the constants from the mean in this case is 4%, and is to be ascribed to the fact that the vapor pressures are high, thus making the attainment of equilibrium less certain. As will appear later, the free energy change attending the solution of chlorine as calculated from these results is in good agreement with that obtained from solubilities and distribution experiments.

With the aid of the above results, data obtained from the literature, and the well-known thermodynamic relation $\Delta F^\circ = -RT \ln K$, the free energy of formation of iodine monochloride in carbon tetrachloride solution may be calculated.

$$\tfrac{1}{2}I_2(g) + \tfrac{1}{2}Cl_2(g) = ICl(g) \qquad \Delta F^\circ_{298} = -3685 \text{ cal.}^{1,12} \qquad (1)$$

$$\tfrac{1}{2}I_2(\text{in } CCl_4) = \tfrac{1}{2}I_2(g) \qquad \Delta F^\circ_{298} = 985 \text{ cal.}^{8} \qquad (2)$$

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(7) Yost, Anderson and Skoog, THIS JOURNAL, 55, 552 (1933).

(8) See Reference 2 and Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 522.

$$\tfrac{1}{2}Cl_2(\text{in } CCl_4) = \tfrac{1}{2}Cl_2(g) \qquad \Delta F^\circ_{298} = -555 \text{ cal.} \qquad (3)$$

$$ICl(g) = ICl(\text{in } CCl_4) \qquad \Delta F^\circ_{298} = -763 \text{ cal.} \qquad (4)$$

Hence

$$\tfrac{1}{2}I_2(\text{in } + CCl_4) + \tfrac{1}{2}Cl_2(\text{in } CCl_4) = ICl(\text{in } CCl_4), \ \Delta F^\circ_{298} = -4018 \pm 50 \text{ cal.} \qquad (5)$$

It is seen that the standard free energy decrease attending reaction (5) is greater than that for reaction (1), although the difference is not large. In the case of iodine monobromide the free energy changes for the corresponding reactions differ by only 50 cal.[7]

The standard free energy change attending reaction (3), −555 cal., is very nearly that calculated from solubility measurements,[9] −546 cal., and does not deviate greatly from the value, −515 cal., obtained by Lewis and Randall (*loc. cit.*, p. 502) from the solubility of chlorine in water and distribution ratios.

The equilibrium constant for reaction (5) is 812 at 25.0°, and is independent of the units used to express the concentrations since there is no change in the number of molecules when the reaction takes place. The degree of dissociation of iodine monochloride in carbon tetrachloride solution at 25.0° is 0.25%, while in the gas phase it is 0.42%.[1]

Results of Thermochemical Measurements.—In Tables III, IV, V, VI and VII are presented representative results of the measurements on heats of solution and formation of iodine, bromine, iodine monochloride, iodine monobromide and bromine monochloride in carbon tetrachloride.

TABLE III

HEAT OF SOLUTION OF IODINE IN CARBON TETRACHLORIDE AT 25°

I_2(s) in g./liter CCl_4	4.270	5.060	5.275	5.277	5.366	5.519	5.618	5.645	5.748	6.246	6.661
Heat of soln. in cal./mole I_2	−5970	−6060	−5950	−5910	−5960	−6010	−6090	−5990	−5900	−6180	−5910
Mean	−5990 ± 60 cal.										

TABLE IV

HEAT OF SOLUTION OF BROMINE IN CARBON TETRACHLORIDE AT 25°

Br_2(l) in g./liter CCl_4	8.109	10.938	11.525	14.362	14.965
Heat of soln., cal./mole Br_2	−730	−698	−710	−705	−718
Mean	−712 ± 10 cal.				

These results show that the heats of solution of iodine and bromine, are within the limits of experimental error, independent of the final concentration attained, and hence the heats of dilution are small. This behavior is to be expected of solutions which are perfect or nearly perfect.

TABLE V

HEAT OF FORMATION OF IODINE MONOCHLORIDE IN CARBON TETRACHLORIDE SOLUTION

$\tfrac{1}{2}I_2(\text{IN } CCl_4) + \tfrac{1}{2}Cl_2(\text{IN } CCl_4) = ICl(\text{IN } CCl_4)$

I_2(s) in g./liter CCl_4	5.563	5.741	6.013	6.230	7.269	8.722
Heat of formation, cal./mole ICl	3980	3960	3980	3960	3970	3990
Mean	3970 ± 30 cal.					

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[9] Taylor and Hildebrand, THIS JOURNAL, 45, 682 (1923).

TABLE VI

HEAT OF FORMATION OF IODINE MONOBROMIDE IN CARBON TETRACHLORIDE SOLUTION

$\frac{1}{2}I_2(\text{in } CCl_4) + \frac{1}{2}Br(\text{in } CCl_4) = IBr(\text{in } CCl_4)$

$I_2(s)$ in g./liter CCl_4	4.363	4.727	5.310	5.313	5.418	5.639	5.665
Heat of formation, cal./mole IBr	1630	1670	1600	1630	1610	1620	1630
Mean	1630 ± 30 cal.						

TABLE VII

HEAT OF FORMATION OF BROMINE MONOCHLORIDE IN CARBON TETRACHLORIDE SOLUTION. $\frac{1}{2}Br_2(\text{in } CCl_4) + \frac{1}{2}Cl_2(\text{in } CCl_4) = BrCl(\text{in } CCl_4)$

$Br_2(l)$ in g./liter CCl_4	11.867	13.442	13.556	15.517	22.276
Heat of formation, cal./mole BrCl	363	374	391	392	372
Mean	378 ± 10 cal.				

Since the measurements on the heats of formation of iodine monochloride, iodine monobromide and bromine monochloride were carried out by adding solid iodine or liquid bromine to solutions of chlorine or bromine in carbon tetrachloride, it was necessary, in arriving at the values given in Tables V, VI and VII, to take into account the heat of solution of the iodine and bromine given in Tables III and IV. It was assumed, in accordance with the results of the experiments on heats of solution, that the heats of dilution involved are small. Moreover, since the halogens and interhalogen compounds are similar in nature, and since there is no change in the number of molecules accompanying the formation of the interhalogen compounds, the small heats of dilution in all probability cancel each other. The results given in Tables V, VI and VII may therefore be regarded as partial molal heats of reaction.

In Table VII the values for the heat of formation of bromine monochloride in carbon tetrachloride have been corrected for the degree of dissociation as calculated from the mean, 0.3, of the equilibrium constants found by Barratt and Stein[10] for the reaction $2BrCl(\text{in } CCl_4) = Br_2(\text{in } CCl_4) + Cl_2(\text{in } CCl_4)$.

In making the measurements of this heat of formation it was found that the reaction involved is a relatively slow one. After adding the bromine to the solution of chlorine in carbon tetrachloride, from ten to fifteen minutes was required for the temperature to reach a maximum, whereas for the analogous reactions to form iodine monochloride and iodine monobromide four to six minutes was required.

It is not convenient to determine directly the heat of solution of chlorine, and this quantity was calculated from the data of Taylor and Hildebrand[9] on the temperature variation of the solubility of the gas in carbon tetrachloride. This quantity, −3720 cal., is, of course, the partial molal heat of solution, but will not differ greatly from the total heat of solution since the solutions are nearly perfect. A similar calculation for the case of iodine gave a result which compared favorably with the values given in Table III.

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(10) Barratt and Stein, *Proc. Roy. Soc.* (London), A122, 582 (1929).

The following chemical equations together with the corresponding changes in free energy, heat content, entropy and degree of dissociation α may be written

$\frac{1}{2}I_2(\text{in } CCl_4) + \frac{1}{2}Cl_2(\text{in } CCl_4) = ICl(\text{in } CCl_4)$ (6)
$\Delta H^\circ_{298} = -3970$ cal. $\Delta F^\circ_{298} = -4018$ cal. $\Delta S^\circ_{298} = 0.16$ cal./deg. $\alpha = 0.25\%$
$\frac{1}{2}I_2(\text{in } CCl_4) + \frac{1}{2}Br_2(\text{in } CCl_4) = IBr(\text{in } CCl_4)$ (7)
$\Delta H^\circ_{298} = -1630$ cal. $\Delta F^\circ_{298} = -1746$ cal. $\Delta S^\circ_{298} = 0.39$ cal./deg. $\alpha = 9.5\%$
$\frac{1}{2}Br_2(\text{in } CCl_4) + \frac{1}{2}Cl_2(\text{in } CCl_4) = BrCl(\text{in } CCl_4)$ (8)
$\Delta H^\circ_{298} = -349$ cal. $\Delta F^\circ_{298} = -357$ cal. $\Delta S^\circ_{298} = 0.025$ cal./deg. $\alpha = 52.4\%$

In each case the entropy change is smaller than for the corresponding gas reaction, 1.36 cal./deg., 1.51 cal./deg. and 1.11 cal./deg., respectively.

Further, the following equations may be written

$ICl(g) = \frac{1}{2}I_2(g) + \frac{1}{2}Cl_2(g)$ $\Delta H^\circ_{298} = 3280$ cal.[1]
$\frac{1}{2}Cl_2(g) = \frac{1}{2}Cl_2(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -1860$ cal.
$\frac{1}{2}I_2(g) = \frac{1}{2}I_2(s)$ $\Delta H^\circ_{298} = -7438$ cal.[1]
$\frac{1}{2}I_2(s) = \frac{1}{2}I_2(\text{in } CCl_4)$ $\Delta H^\circ_{298} = 2995$ cal.
$\frac{1}{2}I_2(\text{in } CCl_4) + \frac{1}{2}Cl_2(\text{in } CCl_4) = ICl(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -3970$ cal.

Hence

$ICl(g) = ICl(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -6993$ cal.

and since $\Delta F^\circ_{298} = -763$ cal., $\Delta S^\circ_{298} = -20.9$ cal./deg. If the value 59.2 cal./deg.[1] is used for the standard absolute entropy of gaseous iodine monochloride at 25.0° the absolute entropy of the compound in carbon tetrachloride solution becomes 38.3 cal./deg. This value refers to a hypothetical solution in which the mole fraction of iodine monochloride is unity. Similarly

$IBr(g) = \frac{1}{2}I_2(g) + \frac{1}{2}Br_2(g)$ $\Delta H^\circ_{298} = 1372$ cal.[11]
$\frac{1}{2}Br_2(l) = \frac{1}{2}Br_2(\text{in } CCl_4)$ $\Delta H^\circ_{298} = 356$ cal.
$\frac{1}{2}Br_2(g) = \frac{1}{2}Br_2(l)$ $\Delta H^\circ_{298} = -3795$ cal.[8]
$\frac{1}{2}I_2(g) = \frac{1}{2}I_2(s)$ $\Delta H^\circ_{298} = -7438$ cal.
$\frac{1}{2}I_2(s) = \frac{1}{2}I_2(\text{in } CCl_4)$ $\Delta H^\circ_{298} = 2995$ cal.
$\frac{1}{2}I_2(\text{in } CCl_4) + \frac{1}{2}Br_2(\text{in } CCl_4) = IBr(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -1630$ cal.

Hence

$IBr(g) = IBr(\text{in } CCl_4)$ $\Delta H^\circ_{298} = -8140$ cal.

and since $\Delta F^\circ_{298} = -1124$ cal., $\Delta S^\circ_{298} = -23.5$. The standard absolute entropy of gaseous iodine monobromide[11] at 25° is 62.0 cal./deg., and the absolute entropy in carbon tetrachloride solution becomes 38.3 cal./deg. Here again the standard state is a solution in which the mole fraction of the compound is unity.

To obtain the entropy of bromine monochloride in carbon tetrachloride solution, we write the following equations

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(11) W. G. Brown, *Phys. Rev.*, **42**, 355 (1932), has found spectroscopically that for the reaction $\frac{1}{2}I_2(g) + \frac{1}{2}Br_2(g) = IBr(g)$, $\Delta H = -1372$ cal. This value, combined with the equilibrium data of McMorris and Yost,[8] leads to the free energy equation $\Delta F^\circ = -1372 - 1.51\,T$. It is believed that this spectroscopic value for ΔH is a bit more accurate than the one obtained from the variation of the equilibrium constant with temperature, −1270 cal. The entropy of IBr(g) now becomes 62.0 cal./deg. at 25° and one atmosphere.

$$\tfrac{1}{2}\mathrm{Br_2(in\ CCl_4)} + \tfrac{1}{2}\mathrm{Cl_2(in\ CCl_4)} = \mathrm{BrCl(in\ CCl_4)} \qquad \Delta H^\circ_{298} = -378 \text{ cal.}$$

$$\tfrac{1}{2}\mathrm{Br_2(l)} = \tfrac{1}{2}\mathrm{Br_2(in\ CCl_4)} \qquad \Delta H^\circ_{298} = 356 \text{ cal.}$$

$$\tfrac{1}{2}\mathrm{Cl_2(g)} = \tfrac{1}{2}\mathrm{Cl_2(in\ CCl_4)} \qquad \Delta H^\circ_{298} = -1860 \text{ cal.}$$

$$\tfrac{1}{2}\mathrm{Br_2(g)} = \tfrac{1}{2}\mathrm{Br_2(l)} \qquad \Delta H^\circ_{298} = -3795 \text{ cal.}^{2}$$

Hence

$$\tfrac{1}{2}\mathrm{Br_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} = \mathrm{BrCl(in\ CCl_4)} \qquad \Delta H^\circ_{298} = -5677 \text{ cal.}$$

and since $\Delta F^\circ_{298} = 15$ cal.,[10] $\Delta S^\circ = -19.1$ cal./deg., and the absolute entropy of bromine monochloride in carbon tetrachloride solution becomes 36.9 cal./deg. when the standard absolute entropies of gaseous bromine[1] and chlorine[1] are taken as 58.63 cal./deg. and 53.31 cal./deg., respectively, at 25.0°.

The Thermodynamic Constants of the Halogens and Interhalogen Compounds in Carbon Tetrachloride Solution.—The results of the determinations and calculations made, together with the entropies of the gaseous halogens and interhalogen compounds, are presented in Tables VIII and IX in a conveniently usable form.

TABLE VIII

THERMODYNAMIC CONSTANTS OF THE GASEOUS HALOGENS AND INTERHALOGEN COMPOUNDS AT 25°

Substance	I_2(g)	Br_2(g)	Cl_2(g)	ICl(g)[12]	IBr(g)	BrCl(g)
Ref. subs.	I_2(s)	Br_2(l)	Cl_2(g)	I_2(s) Cl_2(g)	I_2(s) Br_2(l)	Br_2(l) Cl_2(g)
Free energy	4630	755	0	−1370	971	−251[13]
Heat content	14876	7590	0	4158	9861	(3495)[14]
Entropy[a]	62.29	58.63	53.31	59.15	62.0	(57.1)[14]

[a] These are the standard absolute entropies of the substances given in the first row of the table.

TABLE IX

THERMODYNAMIC CONSTANTS OF THE HALOGENS AND INTERHALOGEN COMPOUNDS IN CARBON TETRACHLORIDE SOLUTION AT 25°

Substance	I_2(in CCl_4)	Br_2(in CCl_4)	Cl_2(in CCl_4)	ICl(in CCl_4)	IBr(in CCl_4)	BrCl(in CCl_4)
Ref. subs.	I_2(s)	Br_2(l)	Cl_2(g)	I_2(s) Cl_2(g)	I_2(s) Br_2(l)	Br_2(l) Cl_2(g)
Free energy	2660	389	1110	−2133	−153	393
Heat content	5990	712	−3720	−2835	1721	−1882
Entropy[a]	39.1	36.8	37.1	38.3	38.5	36.9

[a] These are the standard absolute entropies of the substances given in the first row of the table.

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(12) In Table IV of the article by McMorris and Yost the values for the free energies and entropies of ICl(g), ICl(l) and ICl(s) in the last three columns are in error. The error arose from using twice the free energy value for the reaction $^1/_2I_2(s) = {}^1/_2I_2(g)$ instead of the correct one of 4620 cal. The corrected values given in this paper were obtained by using the spectroscopically determined free energy equation $\Delta F^\circ = -3280 - 1.36\,T$ for the reaction $^1/_2I_2(g) + {}^1/_2Cl_2(g) = ICl(g)$, since it is in essential agreement with that determined from equilibrium measurements and is probably less subject to error.

(13) The equilibrium constant obtained by Murdoch (Ref. 3) for the reaction $2BrCl(g) = Br_2(g) + Cl_2(g)$ is 0.12, and this value was used to calculate the above free energy change.

(14) In the case of both iodine monochloride and iodine monobromide it was found that the heats of formation of the gaseous compound from the gaseous elements are about 20% less than those for the corresponding reactions with all substances in carbon tetrachloride; accordingly, the heat of the reaction $^1/_2Br_2(g) + {}^1/_2Cl_2(g) = BrCl(g)$ was assumed to be 300 cal., and the above heat content and entropy calculated using this value.

It will be noted that the entropies of both the halogens and the interhalogen compounds in carbon tetrachloride solution do not differ greatly from each other; this is not the case for the gases.

Summary

The partial vapor pressures of iodine monochloride and chlorine above their carbon tetrachloride solutions have been measured and from the results, combined with those of other investigators, the free energy of formation of the monochloride in solution has been calculated.

Determinations of the heats of solution of iodine and bromine in carbon tetrachloride and the heats of formation of iodine monochloride, iodine monobromide and bromine monochloride in the same solvent have been made. These data were combined with the known free energy values to obtain the thermodynamic constants of the halogens and interhalogen compounds in their carbon tetrachloride solutions. The values are collected in Table IX, and in Table VIII are presented the corresponding data for the same substances in the gas phase.

It was found that the reaction between bromine and chlorine in carbon tetrachloride solution is appreciably slower than the corresponding reactions between iodine and chlorine and iodine and bromine.

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The Thermodynamics of Ionized Water in Potassium and Sodium Bromide Solutions

BY HERBERT S. HARNED AND WALTER J. HAMER

Recently considerable information regarding the behaviors of the ions of water in potassium and lithium chloride solutions from electromotive force measurements of cells without liquid junction has been obtained.[1] This study has now been extended to include similar data and calculations of related properties in potassium and sodium bromide solutions. To this end, measurements of the cells

$$\mathrm{H_2} \mid \mathrm{MOH}(m_0),\ \mathrm{MBr}\ (m) \mid \mathrm{AgBr} \mid \mathrm{Ag}, \quad \text{and} \qquad \text{(A)}$$

$$\mathrm{H_2} \mid \mathrm{HBr}\ (m_0),\ \mathrm{MBr}\ (m) \mid \mathrm{AgBr} \mid \mathrm{Ag} \qquad \text{(B)}$$

have been made throughout a temperature range of from 0 to 60°, where M represents potassium or sodium.

Much valuable information may be obtained from these data of which we have included (1) the ionization constant of water; (2) the normal potential, E_0, of the silver–silver bromide electrode; (3) the activity coefficient of hydrobromic acid in potassium and sodium bromide solutions; (4) the ionic activity coefficient product of water in potassium and sodium bromide solutions; (5) the dissociation of water in potassium and sodium bromide solutions; (6) the partial molal heat content of hydrobromic acid in potassium and sodium bromide solutions; (7) the heat of ionization of water and the partial molal heat of ionization of water in potassium and sodium bromide solutions. All these quantities have been determined throughout the temperature range of 0 to 60°.

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(1) (a) Harned and Hamer, THIS JOURNAL, 55, 2194 (1933); (b) Harned and Copson, *ibid.*, 55, 2206 (1933).

The only earlier investigation of a similar nature is that of Harned and James, who computed the ionic activity coefficient and dissociation of water at 25° in these solutions from measurements of three cells, of which two contained amalgam electrodes. These results were found to be good but far less extensive than the present series of measurements.[2]

Experimental Results

The apparatus employed was identical with that previously described by us. Vacuum technique and air-free solutions were employed. The same procedure was adopted in preparing the electrodes, except that in the case of the silver-silver bromide electrode the additional precaution of excluding light during their preparation was taken. The apparatus was painted black and the electrodes never turned dark. Freshly prepared electrodes were used in each cell. Constant boiling highest grade hydrobromic acid was twice distilled and diluted with conductivity water. This solution was analyzed gravimetrically. Potassium and sodium bromides were twice crystallized and dried at 110°. The salts were weighed and introduced into the solutions. Other details were carried out in the manner previously described by us.

Since the cell measurements were very extensive, we have expressed them by means of the linear equations

$$\left.\begin{aligned} E_A &= E_{25} + c(t - 25) + d(t - 25)^2 \\ E_B &= E_{25} + a(t - 25) + b(t - 25)^2 \end{aligned}\right\} \qquad (1)$$

and have recorded the constants E_{25}, a, b, c and d in Table I. Suffice it to say that four cells were measured at 5° temperature intervals throughout the temperature range of 0 to 60° and at each of the eleven salt concentrations recorded. This was done for each of the acid and hydroxide cells designated in the table. The actual over-all reproducibility of these cells was found to be ±0.08 mv. The mean deviation of the mean experimental values from those calculated by equation (1) was found to be ±0.03 mv.

The Ionization Constant of Water.—As a check upon the accuracy of both types of cells and the bromide electrode, we have determined the ionization constant of water, K, by the method previously described by us

(2) Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

TABLE I

CONSTANTS OF EQUATION (1), $E_A = E_{25} + c(t - 25) + d(t - 25)^2$; $E_B = E_{25} + a(t - 25) + b(t - 25)^2$. VALID FROM 0 TO 60°

I. KBr

	Cell (A) H$_2$ | KOH (0.01), KBr (m) | AgBr | Ag			Cell (B) H$_2$ | HBr (0.01), KBr (m) | AgBr | Ag		
$\mu = m + 0.01$	E_{25}	$c \times 10^6$	$d \times 10^6$	E_{25}	$a \times 10^6$	$b \times 10^6$
0.01	.....	.....	.....	0.31355	291.91	−2.818
.02	0.89968	292.0	0.29	.29759	243.91	−2.818
.03	.88194	235.5	.275	.28844	218.09	−2.782
.04	.87161	202.0	.27	.28198	198.17	−2.765
.06	.85849	160.0	.26	.27281	166.27	−2.745
.11	.84096	99.0	.25	.25948	130.82	−2.636
.21	.82343	48.2	.036	.24509	89.45	−2.509
.51	.80019	− 25.2	− .036	.22460	32.82	−2.236
1.01	.78408	− 74.6	− .145	.20625	− 8.45	−2.090
1.51	.77461	−110.8	− .16	.19400	− 39.36	−1.872
2.01	.76743	−137.3	− .25	.18309	− 56.91	−1.781
3.01	.75686	−171.5	− .29	.16584	− 86.27	−1.654

II. NaBr

	Cell (A) H$_2$ | NaOH (0.01), NaBr (m) | AgBr | Ag			Cell (B) H$_2$ | HBr (0.01), NaBr (m) | AgBr | Ag		
$\mu = m + 0.01$	E_{25}	$c \times 10^6$	$d \times 10^6$	E_{25}	$a \times 10^6$	$b \times 10^6$
0.01	.....	.....	.....	0.31335	291.9	−2.818
.02	0.89947	289.0	0.26	.29737	243.9	−2.818
.03	.88160	233.0	.25	.28810	218.0	−2.800
.04	.87117	199.0	.22	.28172	198.2	−2.763
.06	.85793	151.0	.18	.27262	170.3	−2.745
.11	.83989	92.8	.16	.25895	128.7	−2.654
.21	.82160	44.55	.11	.24391	87.5	−2.509
.51	.79688	− 13.63	.073	.22190	38.8	−2.236
1.01	.77718	− 72.0	.00	.20133	0.0	−2.109
1.51	.76484	−104.4	− .073	.18591	− 18.2	−2.036
2.01	.75556	−136.7	− .13	.17327	− 33.4	−1.890
3.01	.74056	−177.0	− .29	.15117	− 44.8	−1.763

which does not involve a knowledge of the normal potential of the silver–silver bromide electrode, E_0. Equation (16) of our earlier communication is

$$E_B - E_A + \frac{RT}{NF}\ln\frac{m''_H m''_{Br} m'_{OH}}{m'_{Br}} - \frac{2RT}{NF}\left(\frac{5.908 \times 10^6}{D^{3/2}\,T^{3/2}}\right)\sqrt{\mu} = \frac{RT}{NF}\ln K - \beta\mu \qquad (2)$$

We plotted the left side of this equation against μ from the data of both the cells containing potassium bromide and sodium bromide, respectively. By extrapolation to zero μ, K was obtained and was found to agree within the estimated order of accuracy (±0.04 mv.) with the values obtained from the cells containing potassium and lithium chloride and contained in Table III of our earlier communication. This agreement leads us to have considerable confidence in the present results.

The Normal Electrode Potential of the Silver–Silver Bromide Electrode.—The electromotive forces of cells of type B, E_B, are given by the equation

$$E_B + \frac{RT}{NF}\ln m_H m_x = E_0 - \frac{RT}{NF}\ln \gamma_H\gamma_x \qquad (3)$$

If we substitute for $\ln \gamma_H\gamma_x$ its value derivable from the limiting law of the theory of Debye and Hückel with an additional linear term, $\beta\mu$, and rearrange, we obtain

$$E_B + \frac{RT}{NF}\ln m_H m_x - \frac{8.324 \times 10^6\, RT}{D^{3/2}\, T^{3/2}\, NF}\sqrt{\mu} = E_0 - \frac{2RT}{NF}\beta\mu \qquad (3)$$

which is equation (6) given by Harned and Copson.[1b] If the left side of this equation is plotted against μ, its value at zero μ is E_0. A plot of this function is given in Fig. 1 of the paper by Harned and Copson for the case of the cell containing hydrochloric acid and lithium chloride. Their values of E_0 agreed to within ±0.04 mv. with those obtained by Harned and Ehlers,[3] who employed the cell containing hydrochloric acid and no salt. Since the activity coefficient of hydrochloric acid in lithium chloride solutions is very nearly the same as its value in pure water at concentrations from 0.01 to 0.1 M, this case is most favorable and close agreement is to

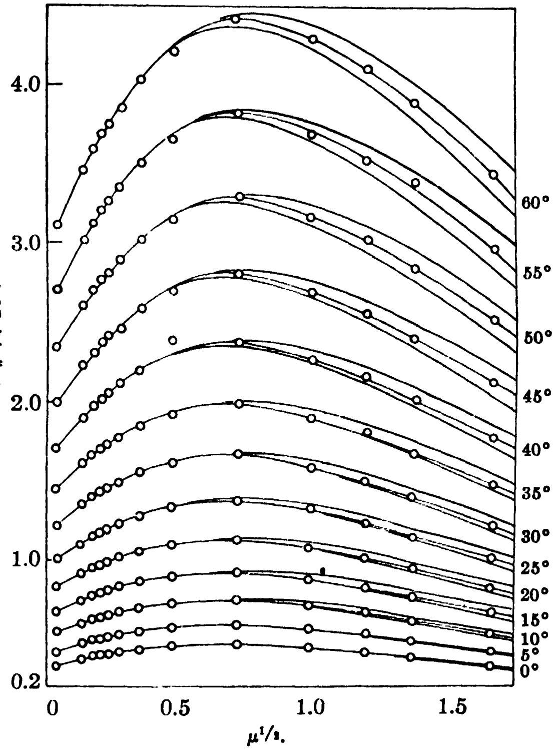

Fig. 1.—The dissociation of water in potassium chloride and bromide and sodium bromide solutions.

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(3) Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933).

be expected. On the other hand, the activity coefficient of the hydrochloric acid in potassium chloride solutions becomes less than its value in pure aqueous solution in this region of concentration, particularly at the higher temperatures, a fact which is also true of hydrobromic acid in potassium bromide solutions and to a less degree of hydrobromic acid in sodium bromide solutions. Therefore, if we employ this method of extrapolation with the hydrochloric acid cells containing potassium chloride and draw the plot through the 0.01 *M* point, we can predict that the values of E_0 thus derived will be slightly lower than those obtained by Harned and Ehlers. This indeed was found to be the case. Very close agreement was found to occur at the lower temperatures but an increasing deviation occurs as the temperature increases, becoming 0.08 mv. at 25° and 0.14 mv. at 60°. Since this is the maximum deviation to be expected, we have confidence that the normal potential of the silver–silver bromide electrode may be evaluated to within 0.1 mv. by this method. This has been done for the cells containing both potassium and sodium bromide and the values obtained are given in the third and fourth columns of Table II. It should be noted that the values derived from the cells containing the potassium salt are about 0.05 mv. lower than those from the cells containing the sodium salt.

As a further interesting confirmation and also a test of the general consistency of the cells, we have resorted to a method of determining E_0 from the electromotive forces of the cells containing potassium hydroxide and bromide. The equation for cells of the type (A) is[4]

$$E_A - E_0 + \frac{RT}{NF}\ln\frac{m_{Br}}{m_{OH}} = \frac{RT}{NF}\ln\frac{\gamma_H\gamma_{OH}}{\gamma_H\gamma_{Br}\,a_{H_2O}} - \frac{RT}{NF}\ln K \qquad (4)$$

At the lower concentrations, the activity coefficient ratio may be taken to be unity. Therefore, if we employ cells in which the ratio of m_{Br} to m_{OH} is unity, we obtain

$$E_A + (RT/NF)\ln K = E_0 \qquad (5)$$

The electromotive forces of the cells containing 0.01 *M* hydroxide and bromide were used as well as the values of *K*, the ionization constant of water contained in Table III of our earlier communication. The values of E_0 thus derived are given in the second column of Table II. These were averaged with those obtained from the two acid cells and this average is given in the fifth column of the table. These average results were then subjected to the method of least squares whence the equation

$$E_0 = 0.07169 - 5.259 \times 10^{-4}(t - 25) - 3.022 \times 10^{-6}(t - 25)^2 \qquad (6)$$

was obtained. The deviations between the values computed by equation (6) and $E_{av.}$ are given in the last column of the table.

Although this is not so good a method of determining E_0 as that which employs the cells containing the acid alone, the results thus obtained give values of the activity coefficient from the electromotive forces at 0.01 M hydrobromic acid which are quite reasonable and agree closely with similar values obtained for hydrochloric acid throughout the entire temperature range. It should be borne in mind that these are the normal potentials of a silver–silver bromide electrode prepared by heating silver oxide paste and subsequent electrolysis. These values may differ by a few tenths of a millivolt from those obtained with electrodes prepared by some other method. The present results are very consistent and give very reasonable values of the thermodynamic properties.

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(4) Equation (4). Harned and Hamer, Ref. 1.

TABLE II

THE NORMAL POTENTIAL OF THE SILVER–SILVER BROMIDE ELECTRODE

°C.	E_0 (KOH-KBr)	E_0 (HBr-KBr)	E_0 (HBr-NaBr)	E_0 (Mean)	$E_{0\text{calcd.}} - E_0$ (mv.)
0	0.08288	0.08299	0.08301	0.08296	−0.01
5	.08091	.08095	.08100	.08095	+ .05
10	.07884	.07883	.07889	.07885	+ .06
15	.07663	.07660	.07665	.07662	+ .03
20	.07422	.07417	.07422	.07420	+ .03
25	.07172	.07165	.07170	.07169	.00
30	.06905	.06895	.06899	.06900	− .01
35	.06613	.06603	.06607	.06608	+ .05
40	.06311	.06299	.06305	.06305	+ .07
45	.05999	.05986	.05992	.05992	+ .04
50	.05675	.05655	.05660	.05663	+ .02
55	.05328	.05309	.05316	.05318	+ .01
60	.04975	.04955	.04961	.04964	− .06

The Activity Coefficient of Hydrobromic Acid in Potassium and Sodium Bromide Solutions.—From these values of E_0 and by means of the equation for cells of type (B), namely

$$E_B = E_0 - \frac{RT}{NF} \ln m_H m_{Br}\, \gamma_H \gamma_{Br} \qquad (7)$$

the activity coefficient of hydrobromic acid in sodium and potassium bromide solutions was computed. The accuracy is estimated to be ±1 in the third decimal place of activity coefficient. For reasons of brevity and because at the present juncture we wish to emphasize certain novel features calculable from these data, we shall not incorporate the results of these calculations in the present communication.

The Ionic Activity Coefficient and Dissociation of Water in Potassium and Sodium Bromide Solutions.—From the differences in electromotive force, $E_A - E_B$, of the hydroxide–salt and acid–salt cells, the ionic activity coefficient of water in the bromide solutions may be computed by a rearranged form of an equation from our earlier communication, namely[5]

$$\ln \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = (E_A - E_B)\frac{NF}{RT} - \ln \frac{m''_H m''_{Br} m'_{OH}}{m'_{Br}} + \ln K \qquad (8)$$

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[5] Harned and Hamer, THIS JOURNAL, 55, 2194 (1933); Equation (14).

K is the ionization constant of water, m''_{H} and m''_{Br} are the molalities of the hydrogen and bromide ions in the acid cells (B), and m'_{OH} and m'_{Br} those of the hydroxide and bromide ions in the hydroxide cells (A). The values K employed are given in Table III of our previous investigation.

We have not incorporated these values but have computed from them the dissociation of water m_w or $\sqrt{m_H m_{OH}}$ in the bromide solutions by means of the equation

$$m_w = \sqrt{K a_{H_2O}/\gamma_H \gamma_{OH}} \tag{9}$$

Plots of these values are given in Fig. 1. At a given temperature, the top curve shows the effect of sodium bromide, the middle curve that of potassium bromide and the lower curve that of potassium chloride. The order of these effects at 25° verifies the earlier work of Harned and James.[6]

The Relative Partial Molal Heat Contents of the Halide Acids in Uni-univalent Halide Solutions.—In order to compute the partial molal heat content of the acid relative to its value in the 0.01 M solution of hydrobromic acid, use was made of equation (1) in which E_B is expressed as a function of the temperature. By employing the Gibbs–Helmholtz equation in the manner described by Harned and Hamer,[1a] $\overline{H} - \overline{H}_{0.01}$ of hydrobromic acid in potassium and sodium bromide solutions was computed. The values thus determined at the five degree temperature intervals have been expressed by the linear equation

$$\overline{H} - \overline{H}_{0.01} = (\overline{H} - \overline{H}_{0.01})_0 + \alpha t + \beta t^2 \tag{10}$$

in which $(\overline{H} - \overline{H}_{0.01})_0$, α and β are constants, and t is the temperature in degrees centigrade. Values of these constants are given in Table III.

TABLE III

THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF HYDROBROMIC ACID IN POTASSIUM AND SODIUM BROMIDE SOLUTIONS ($\overline{H} - \overline{H}_{0.01}$)

	I. KBr			II. NaBr		
μ	$(\overline{H} - \overline{H}_{0.01})_0$	α	$\beta \times 10^3$	$(\overline{H} - \overline{H}_{0.01})_0$	α	$\beta \times 10^3$
0.01	0	0	0	0	0	0
.02	38	0	0	42	0	0
.03	59	0.50	0.6	73	0.30	0.5
.04	66	0.70	0.8	71	.65	.70
.06	52	1.00	1	82	.83	.95
.11	79	2.41	2	83	2.21	1.9
.21	84	4.02	5	99	3.92	4.5
.51	78	7.46	12	181	7.38	11.5
1.01	170	9.47	15	347	9.07	14.0
1.51	167	12.10	21	553	10.08	17.0
2.01	268	13.31	23	691	12.09	18.0
3.01	422	14.92	25	1083	13.32	24.0

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(6) Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); see also, Harned, *Trans. Am. Electrochem. Soc.*, **51**, 571 (1927); Taylor, "Treatise on Physical Chemistry," 2d edition, 1931, Vol. I, p. 808, D. Van Nostrand Co., New York.

These results as well as those of hydrochloric acid in potassium chloride and lithium chloride solutions recently determined by us and by Harned and Copson are the only reasonably accurate ones of this kind yet determined. Earlier attempts were made by Harned, who determined $(\overline{H} - \overline{H}_{0.1})$ of hydrochloric acid in potassium, sodium and lithium chloride solutions at 25°, and by Harned and Brumbaugh, who determined the same quantity in the alkaline earth chloride solutions. Although these results are of the right magnitude and the effects of the different salts are in the correct sequence, they are far less consistent than the more recently determined values. This is due in part to the reasons that they obtained results at only three temperatures, that the method of computation used by them was less accurate and that they employed calomel electrodes. The more recent results of Harned and Murphy are better but measurements were not made at a sufficient number of temperatures to render the determination of the temperature coefficients with equal precision. The vacuum technique recently employed has also greatly improved the consistency of the measurements.[7]

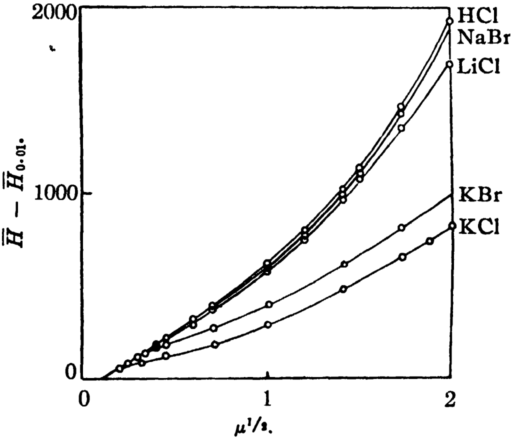

Fig. 2.—The relative partial molal heat content of hydrochloric and hydrobromic acid in their corresponding halide solutions.

In Fig. 2 we have plotted $(\overline{H} - \overline{H}_{0.01})$ of hydrochloric acid,[8] $(\overline{H} - \overline{H}_{0.01})$ of hydrochloric acid in potassium and lithium chloride solutions, and of hydrobromic acid in potassium and sodium bromide solutions at 25°. Although all the experimental points are not shown, the consistency of the results is encouraging. To illustrate, the curve for hydrochloric acid is of the same general form and agrees closely in the more dilute solutions with that of hydrochloric acid in lithium chloride solutions. Further, the formal agreement of these curves with that of hydrobromic acid in sodium bromide solutions should be noted. In fact, the whole system of graphs is consistent. As far as we are able to judge, the results are correct to within ±30 calories, which corresponds to an error in the temperature coefficient of electromotive force of ±0.004 mv. Very similar results are found at all temperatures which have been investigated.

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(7) Harned, THIS JOURNAL, 42, 1808 (1920); Harned and Brumbaugh, *ibid.*, 44, 2729 (1922); Harned and Murphy, *ibid.*, 53, 8 (1931).

(8) Harned and Ehlers, 55, 2179 (1933).

The Total Heat of Ionization of Water in Halide Solutions.—The electromotive force, $E_B - E_A$, of the double cell

$$H_2 \mid MOH\ (0.01),\ MX\ (m) \mid AgX \mid Ag \mid AgX \mid MX\ (m),\ HX\ (0.01) \mid H_2$$

where M represents potassium or sodium and X represents chloride or bromide, is given by equation (8) in the form

$$(E_B - E_A) = -\frac{RT}{F}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}} - \frac{RT}{F}\ln\frac{m''_H m''_X m'_{OH}}{m'_X} + \frac{RT}{F}\ln K \qquad (11)$$

The cell reaction is simply that of the dissociation of water into ions. If this value of $(E_B - E_A)$ be substituted in the Gibbs–Helmholtz equation, we obtain

$$\Delta H = RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T} - RT^2\left(\mathrm{d}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}\middle/\mathrm{d}T\right) \qquad (12)$$

The first term on the right equals the heat content of ionization at zero salt concentration, ΔH_i, while the second term on the right is the partial molal heat content of the hydrogen and hydroxyl ions, $\Delta\overline{H}$, in the salt solution of a given strength. Thus, ΔH is the total heat content of ionization.

ΔH was computed from the electromotive forces by employing equations (1) and the Gibbs–Helmholtz equation. The equation thus derived is

$$\Delta H = -F(E_B - E_A)_{25} - FT(\mathrm{A}) + F[(\mathrm{A}) - 2T(\mathrm{B})](t - 25) + F(\mathrm{B})(t - 25)^2 \quad (13)$$

where $(E_B - E_A)_{25}$ are the differences in electromotive forces at 25°, t is °C., (A) equals $(c - a)$, and (B) equals $(d - b)$. The values of ΔH thus obtained at the different salt molalities were then plotted as illustrated in Fig. 3. As far as may be determined from these results the plots are straight lines. Judging from other results of a similar nature, we do not regard this as strictly true but merely as a first approximation. The deviations of the points from the lines were within ±50 cal. with very few exceptions and considerably less than this for the majority of the results. The results were then least squared at constant temperatures using the equation for a straight line, namely

$$\Delta H = \Delta H_i + \omega\mu^{1/2} \qquad (14)$$

The constants of this equation are given in Table IV. These computations were made with three independent series of data which give us the total heat of ionization of water in potassium chloride and bromide solutions and in sodium bromide solutions. Consequently, each heat of ionization, ΔH_i, was determined independently. The average values of the three determinations are given in the table. The results are quite good since this determination involves the combined errors of both the acid and hydroxide cells. By the method of least squares, the equation for ΔH_i

$$\Delta H_i = 20{,}182 + 0.026117T - 0.078067T^2 + 0.0000079127T^3 \qquad (15)$$

was obtained. Deviations of the observed results from those computed by this equation are shown in the last column of the table.

Previously, we evaluated K directly and calculated ΔH_i from K. The values of ΔH_i obtained by the present method and given by equation (14) are in all probability of greater accuracy through the entire range of temperature than the former ones computed by the indirect method.

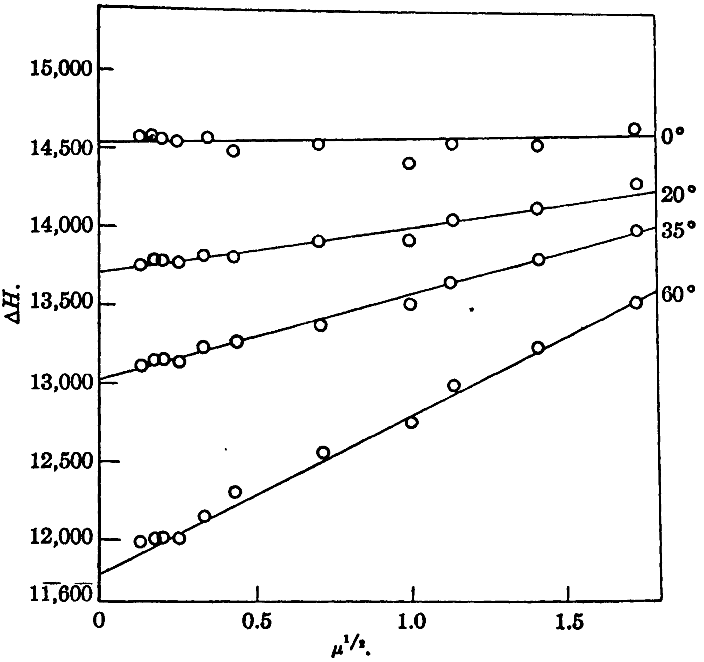

Fig. 3.—The total heat content of ionization of water in potassium bromide solutions.

From 0 to 30°, however, the agreement between the values obtained by both methods is excellent and the deviation is less than 0.3%. At 35, 40,

TABLE IV

CONSTANTS OF EQUATION (14) AND HEAT OF IONIZATION OF WATER IN CALORIES

	(1) KCl		(2) KBr		(3) NaBr			
t, °C.	ΔH_i	ω	ΔH_i	ω	ΔH_i	ω	ΔH_i(av.)	Δ^a
0	14,567	85.9	14,531	4.8	14,472	162.3	14,523	+5
5	14,365	143.3	14,326	71.8	14,283	217.8	14,325	−3
10	14,139	215.7	14,121	143.6	14,079	283.5	14,113	0
15	13,921	279.8	13,906	226.3	13,871	350.4	13,899	+1
20	13,699	345.3	13,693	303.7	13,660	471.1	13,684	−2
25	13,488	401.2	13,472	386.2	13,445	486.3	13,468	−5
30	13,235	485.5	13,242	472.9	13,226	556.9	13,234	+7
35	12,997	553.1	13,023	551.5	13,016	619.8	13,012	0
40	12,768	622.8	12,794	635.1	12,778	700.2	12,780	+2
45	12,526	694.9	12,569	715.0	12,548	744.7	12,538	+8
50	12,279	772.2	12,334	800.8	12,316	848.0	12,310	−2
55	12,030	843.2	12,084	896.3	12,079	927.6	12,064	+3
60	11,777	916.1	11,849	969.0	11,849	995.4	11,825	−4

[a] $\Delta = \Delta H_{i\,(\text{Eq. 15})} - \Delta H_{i\,(\text{av.})}$.

45, 50, 55, and 60° the deviations are 0.3, 0.4, 0.5, 0.6, 0.8, and 1%, respectively. The new values at these temperatures are in all cases lower than the previously determined ones. We may sum up by saying that our best values for ΔH_i are given by equation (14), and our best values for K are the observed ones in Table III of our former contribution.

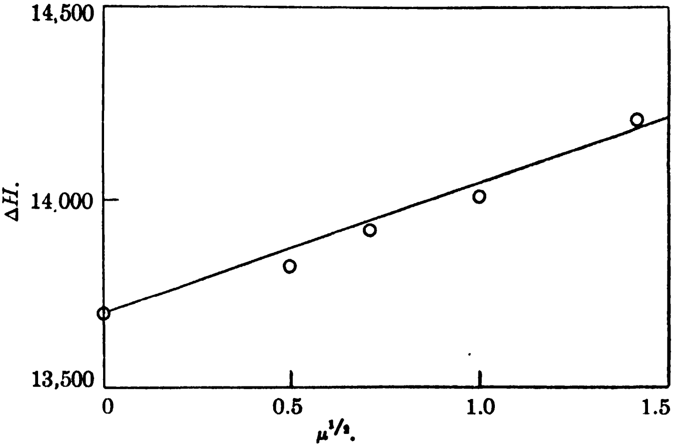

Fig. 4.—The total heat content of ionization of water in potassium chloride solutions from electromotive forces and calorimetric data.

In Fig. 4, we have drawn our plot of the total heat of ionization of water, ΔH, in potassium chloride solutions at 20° against $\mu^{1/2}$. Fortunately, the same quantity was determined directly by calorimetric measurements of the heat of neutralization of hydrochloric acid and potassium hydroxide by Richards and Rowe.[9] Their results are shown by the circles. At 0.25, 0.5, 1 and 2 μ, the agreement is within 53, 38, 30 and −24 cal., respectively. Their extrapolated value would be approximately 40 cal. lower than ours if they had employed a straight line function for the purposes of extrapolation. We consider this agreement which is within 0.3% as excellent confirmation of the method which we have employed to evaluate these quantities.[10]

As previously mentioned the partial molal heat contents, $\Delta\overline{H}$, of the hydrogen and hydroxide ions in potassium and sodium bromide and potassium chloride solutions may be computed by the equation

$$\Delta\overline{H} = \omega\sqrt{\mu}$$

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[9] Richards and Rowe, THIS JOURNAL, 44, 684 (1922).

[10] Rossini [*Bur. Standards J. Research*, 6, 847 (1931)] has recently given an equation for ΔH_i. Although the value computed by this equation agrees with ours at 15°, discrepancies occur at other temperatures. We believe that a considerable part of this lack of agreement is due to uncertainties in the values of $\overline{C}p_0$ of NaCl, HCl, and NaOH which were combined to compute ΔCp of the dissociation of water. Thus, Rossini computes 57.9 cal. for ΔCp at 18° while we find approximately 44 cal. The more recent values of $\overline{C}p_0$ of HCl and NaOH at 25° obtained by Gucker and Schminke [THIS JOURNAL, 54, 1358 (1932); 55, 1013 (1933)] give a value for ΔCp at 25°, 6 cal. lower than that of Rossini if we employ the value of $\overline{C}p_0$ of NaCl given by Rossini. It seems improbable that our values of ΔH_i can be in error to the above extent since we have obtained excellent agreement with calorimetric data at 20° at which temperature accurate heats of neutralization have been measured.

from the values of ω given in Table IV with an estimated accuracy in the middle range of temperatures of about ±30 cal. At the higher and lower temperatures the accuracy is not so good as this but is probably approximately ±50 cal. The evidence derived from these results indicates approximately that $\Delta\overline{H}$ varies linearly with $\mu^{1/2}$.

Summary

1. Measurements of the cells

$$H_2 \mid MOH\ (0.01),\ MBr\ (m) \mid AgBr \mid Ag$$
$$H_2 \mid HBr\ (0.01),\ MBr\ (m) \mid AgBr \mid Ag$$

in aqueous solution from 0 to 60° have been made. M is potassium or sodium.

2. The dissociation constant of water was computed from these results and the values obtained agreed with those previously obtained by us from cells containing hydrochloric acid and potassium chloride.

3. From these cells the values of the normal potential of the silver–silver bromide electrode, E_0, has been computed from 0 to 60° at 5° intervals. These are given by $E_0 = 0.07169 - 5.259 \times 10^{-4}(t - 25) - 3.022 \times 10^{-6}(t - 25)^2$ with an accuracy estimated to be ±0.1 mv.

4. Methods are indicated for computing the activity coefficient of hydrobromic acid and the ionic activity coefficient product of water in potassium and sodium bromide solutions.

5. The partial molal heat content of the acid in potassium and sodium bromide solutions from 0 to 60° has been computed and compared with that of hydrochloric acid in chloride solutions.

6. The total heat content of the dissociation of water as well as the relative partial molal heat content of the hydrogen and hydroxide ions in potassium chloride and bromide solutions and sodium bromide solutions from 0 to 60°, have been computed. Good agreement is found with calorimetric data from heats of neutralization at 20°.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Effect of Ethyl Radicals on the Thermal Decomposition of Azomethane. The Kinetics of the Thermal Decomposition of Tetraethyllead. Ethyl Radicals and Hydrogen

BY JOHN A. LEERMAKERS[1]

Certain theories of homogeneous, unimolecular reactions[2] have been quite successful in interpreting the rates of decomposition of a number of compounds.[3] Although the excellent agreement of these theories with experiment, as well as certain experimental observations *per se*, practically excludes the existence of long reaction chains in those reactions which are termed homogeneous and unimolecular, yet there is no definite proof that very short chains do not occur in such reactions. For example, if such short chains did exist and if the chain propagating reactions were very fast compared to the unimolecular reaction and were initiated by it, the unimolecular reaction would be the rate determining step and the over-all reaction would have unimolecular characteristics. It was the purpose of this investigation to obtain experimental evidence for the existence or non-existence of short chains in one well-established homogeneous, unimolecular reaction.

It is not possible to test the existence of short chains by the introduction of surface, since there is no absolute assurance that such short chains would be terminated at that surface. It was thought that information of the kind desired might be obtained by introducing into the gas under investigation the molecular species most probably capable of initiating chains and then observing any acceleration in the rate of decomposition of that gas.

Azomethane, whose thermal decomposition has been quite thoroughly studied,[4] was chosen for this investigation for two reasons. First, the products of its decomposition are quite simple and very stable; and, second, there is good evidence that the decomposition of azomethane results in the liberation of methyl radicals,[5] which might initiate chains by reacting with the undecomposed azomethane.

It was hoped to introduce methyl radicals into a system containing azomethane and then to observe quantitatively any effect due to the radicals reacting with the azo compound. It was considered advisable to carry out the investigation at a temperature at which the azomethane itself slowly decomposes, and was, therefore, necessary to find a substance which would act as a supply of radicals at about 275°. No such material was found which would conveniently produce methyl radicals. Tetraethyllead, however, answers all the requirements except that it gives ethyl rather than methyl radicals. The reactions of methyl and ethyl radicals are practically identical, and the activation energies of reaction between, say, azomethane and the two different radicals, respectively, would probably be almost the same. Hence the results obtained with ethyl radicals can very likely be considered, at least qualitatively, to be the results which would be obtained with methyl radicals. The evidence for the production of ethyl radicals from tetraethyllead is sufficiently well known to make it unnecessary to review the work here.[6]

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[1] National Research Fellow in Chemistry.

[2] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); Kassel, *J. Phys. Chem.*, **32**, 225 (1928); *ibid.*, **32**, 1065 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 114, 118 (1928).

[3] See, for example, Kassel, "The Kinetics of Homogeneous Gas Reactions," the Chemical Catalog Company, New York, 1932.

[4] Ramsperger, THIS JOURNAL, **49**, 912, 1495 (1927).

[5] Leermakers, *ibid.*, **55**, 3499 (1933).

The method of investigation consisted first in measuring the rate of decomposition of tetraethyllead and later measuring the same rate when azomethane was present in the system with the lead compound. The presence of any chains initiated by the ethyl radicals should be manifest by an apparent increase in the rate of decomposition of the tetraethyllead. It was necessary to study the thermal decomposition of tetraethyllead since no quantitative data are known concerning its kinetics. This study will be first described. In addition to the work with azomethane, several experiments were made to see if hydrogen reacts with ethyl radicals. The results of these experiments will be briefly given.

I. The Kinetics of the Thermal Decomposition of Tetraethyllead.—Geddes and Mack,[7] in a study principally concerned with the decomposition of germanium tetraethyl, reported that some preliminary investigations had shown that the thermal decomposition of tetraethyllead was a largely homogeneous reaction. They did not report any rate measurements. Meinert[8] studied the products of the decomposition of tetraethyllead, but did not investigate the kinetics of its decomposition. In the research here reported the kinetics of the decomposition were studied at temperatures of 245.0, 260.0 and 275.0°, and from pressures of 13 to 52 mm.

Apparatus and Materials.—The tetraethyllead was an Eastman product, and was purified by the method recommended by Calingaert.[9] It was further purified by distillation as described below.

The rate of the decomposition was measured by the change of pressure with time at constant volume in the apparatus diagrammatically presented in Fig. 1. C is the reaction vessel of about 210-cc. capacity, which was maintained at the desired constant temperature by the mercury boiler A of the type described by Ramsperger and Waddington.[10] B is a click gage used in measuring the pressures which were read on a mercury manometer. D and E are all-metal, sylphon type, needle valves designed so that they could be heated to 175°; they were vacuum tight. G is the supply of tetraethyllead and F is a small U-trap of about 1.5 cc. capacity. K is the stopcock leading to the usual high vacuum line. In order to keep the volume of the system outside of the thermostat as small as possible all tubing was capillary of 1.5 mm. bore. The valves D and

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(6) For leading references see Rice, Johnston and Evering; THIS JOURNAL, **54**, 3529 (1932).

(7) Geddes and Mack, *ibid.*, **52**, 4372 (1930).

(8) Meinert, *ibid.*, **55**, 979 (1933).

(9) Calingaert, *Chem. Rev.*, **2**, 56 (1925).

THIS JOURNAL, **55**, 214 (1933).

E were enclosed in an asbestos box which was heated electrically to 150° and all of the capillary tubing on the reaction vessel side of E, with the exception of the trap F and the supply G, was heated electrically to 180°. The clicker gage B was also heated to 180°.

Procedure.—In making a run, the cell was brought to the desired temperature by the mercury boiling in A and was thoroughly pumped out through K and E. The trap F was cooled to −78°, the supply G was warmed to about 60° by means of a water-bath, and the valve D was opened. The tetraethyllead distilled into F, where it was condensed. When sufficient liquid had collected, the valve D was closed, the pumping was continued for several minutes, and the valve E was then closed. The cooling bath at F was removed and the trap was quickly warmed with a smoky gas flame until the liquid had vaporized. At this time the stop watch was started and a small electrically heated furnace was placed around F. Pressures in the reaction cell were then read at the desired times, readings being taken at such periods as to give approximately equal pressure increments. During the vaporization of the lead alkyl into the reaction cell a slight amount of decomposition occurred. This was apparently negligible since the ratio of final to initial pressure was fairly constant from experiment to experiment. Initial pressures were obtained by extrapolation where this was necessary; otherwise the initial pressure was assumed to be the pressure of the first reading.

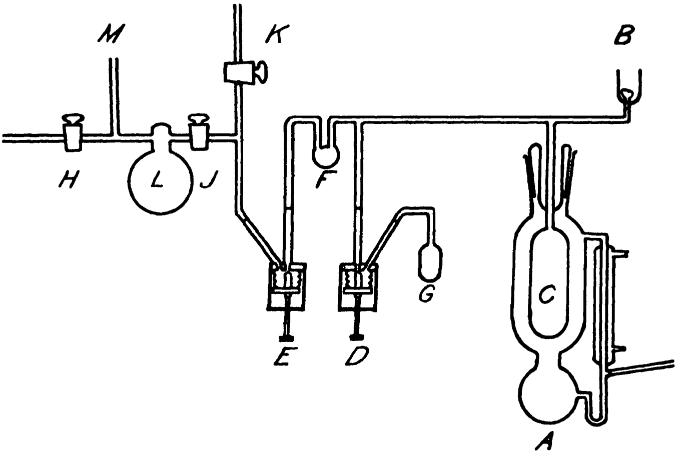

Fig. 1.—Diagram of apparatus used in the experiments.

Experimental Results.—After complete decomposition of tetraethyllead at constant volume the pressure of the products was approximately double the initial pressure of the tetraethyllead. This ratio of final to initial pressure was found to vary somewhat with the temperature of the decomposition. For any given temperature the ratio was fairly constant; the fluctuations were due, probably, to the inaccuracy in the determination of the initial pressure, which resulted from the method of introduction of the lead alkyl into the reaction vessel. At 275.0° the average ratio of final to initial pressure was 2.00, at 260.0° the average ratio was 2.19, and at 245.0° the average ratio was 2.14. From Meinert's data,[8] the ratio of final to initial pressure at 275.0° is calculated to be 1.9. The agreement of the present data with this figure is satisfactory when it is considered that the surface of the reaction vessel used by Meinert was clean glass, while the surface here used was the lead mirror formed by successive decompositions. It is entirely possible that the various reactions involving the radicals would occur to a different extent on the two different surfaces.

Due to the uncertainty in the initial pressures, decomposition was allowed to proceed to completion in all of the experiments. First order rate constants were calculated by the interval method, using the equation

$$k_1 = \frac{2.303}{(t_2 - t_1)} \log \frac{(P_f - P_1)}{(P_f - P_2)}$$

where P_f is the final pressure and P_1 and P_2 are the total pressures at times t_1 and t_2, respectively. Rate constants were calculated until decomposition was from 50 to 75% complete. Beyond about 75% decomposition there was a distinct drop in the constants calculated during a run. In several cases there was a slight trend in the constants from the start; this was not common to all of the runs. The percentage deviation of the individual constants from the average constant for a run varied from 2 to 10%, depending on the run; the grand average of such deviations for all the runs was 7.2%. Table I gives the data of a typical experiment.

TABLE I

DATA FOR TYPICAL EXPERIMENT

Expt. no. 6; P_{initial} = 19.0 mm.; P_{final} = 38.8 mm.; T = 275.0°

P_{total}, mm.	$P_{\text{final}} - P_{\text{total}}$, mm.	t, sec.	$k_1 \times 10^4$, sec.$^{-1}$
21.5	17.3	60	22.0
23.3	15.5	110	24.2
24.9	13.9	155	22.6
27.1	11.7	231	18.1
29.9	8.9	382	21.0
33.1	5.7	594	
38.8	0	∞	

Table II is a summary of all the experiments.

TABLE II

SUMMARY OF ALL EXPERIMENTS

Number	Temp., °C.	P_{initial}, mm.	$P_{\text{final}}/P_{\text{initial}}$	$k_1 \times 10^4$, sec.$^{-1}$
8	275.0	52.7	2.06	22.1
9		41.1	1.99	21.8
10		36.1	2.00	23.1
7		20.8	1.87	21.6
6		19.0	2.04	21.6
4	260.0	44.0	2.17	8.42
2		28.0	2.24	8.45
3		22.7	2.27	8.58
1		13.9	2.15	8.51
11		13.2	2.14	8.41
14	245.0	39.8	2.18	3.27
13		25.2	2.05	2.93
15		21.4	2.18	3.06

TABLE II (*Concluded*)

Surface-volume ratio increased 7.5 times

Number	Temp., °C.	P_{initial}, mm.	$P_{\text{final}}/P_{\text{initial}}$	$k_1 \times 10^4$, sec.$^{-1}$
32	275.0	66.6	[a]	28.5
33		58.1	1.98	28.1
31		39.1	2.08	28.5

[a] Ratio not determined because of long extrapolation to initial pressure.

Discussion of the Results.—It is seen from Table I and Table II that the reaction is unimolecular in character. Over the rather narrow pressure range investigated, the rate constants do not decrease with decreasing pressure; it is very probable that the rates have been measured in the so-called high pressure region. In experiments 31, 32 and 33 the surface-volume ratio of the reaction cell was increased 7.5-fold by packing it with Pyrex tubing. In the first experiment with the packed cell, before the surface of the tubing had become coated with lead, the rate was slightly faster than it was found to be in experiments 31, 32 and 33. On the assumption that the rate of any heterogeneous reaction occurring in the system was proportional to the surface, the reaction in the unpacked cell was between 96 and 97% homogeneous. Geddes and Mack[7] reported that the reaction was 98% homogeneous. Because of the slight heterogeneity it was not thought advisable to measure rates at lower pressures.

A plot of reciprocal temperatures against the logarithms of the rate constants gives a very good straight line. From the slope of this line the energy of activation of the reaction is calculated to be 36,900 calories per mole. The rate constants given in Table II are quite accurately represented by the equation $k_1 = 1.2 \times 10^{12}e^{-36,900/RT}$.

It is interesting to note that within the experimental error the factor A, in the equation $k_1 = Ae^{-Q/RT}$, is the same for the decompositions of tetraethyllead and germanium tetraethyl. Geddes and Mack[7] find that A has the value 3×10^{12} sec.$^{-1}$ for the decomposition of germanium tetraethyl, while the present investigation leads to a value of $A = 1.2 \times 10^{12}$ sec.$^{-1}$ for tetraethyllead.

II. Azomethane and Ethyl Radicals

The experimental procedure in this part of the work consisted of measuring the rate of decomposition of tetraethyllead in the presence of azomethane. By making the necessary corrections for the slow decomposition of the azomethane, rate constants for the tetraethyllead decomposition were calculated from the observed pressure changes. In the computations it was assumed that the ratios of final to initial pressures for the tetraethyllead decomposition had the values found in Part I; the final pressures were not used. By this method of calculation any reaction of ethyl radicals with azomethane would result in rate constants which would be greater than those found in Part I. Several of the experiments were allowed to continue until all of the tetraethyllead had decomposed. By correcting for the azomethane decomposition, the final pressures due to the lead compound were found and the final-initial pressure ratios determined. Any reaction of ethyl radicals with azomethane should increase the ratios beyond those found for tetraethyllead when decomposed alone.

Apparatus and Materials.—Azomethane was prepared by the method of Thiele as described by Ramsperger.[4] The material was freed of inert gases by several times expanding into a bulb, freezing down and pumping out non-condensed gases. The tetraethyllead was the same as used in Part I.

The apparatus is shown diagrammatically in Fig. 1. The only additions to the set-up as described in Part I are the two stopcocks J and H, the 300-cc. flask L and the mercury manometer M. The stopcock H leads to the supply of azomethane which was contained in a trap kept at −78°.

Procedure.—Before a run was started, azomethane was allowed to evaporate into the flask L until the desired pressure, as read on the manometer M, was obtained. The stopcock H was then closed. Tetraethyllead was introduced into the reaction vessel and its pressure determined exactly as described in Part I. After the initial reading of the tetraethyllead pressure had been made, the stopcock K was closed and the stopcock J and the valve E were opened. After about five seconds the valve E and the stopcock J were closed, the time being noted. The pressure in the reaction system for this time was read on the manometer M at a convenient later time. The other pressure readings were taken at the desired time intervals by means of the clicker system as previously described. Measurements for the most part were made until about 80% of the tetraethyllead had decomposed. Several experiments were continued until all of the lead alkyl had decomposed.

Experimental Results.—In order to be certain that azomethane did not decompose catalytically on the lead surface of the reaction vessel, several samples of the gas were decomposed under conditions identical with those which existed during the later experiments except that the tetraethyllead was not present. The results, when compared with those of Ramsperger,[4] indicate that there is no appreciably heterogeneous reaction of azomethane on a lead surface at temperatures around 275°. An experiment was performed immediately following those described above to determine if the products of the azomethane decomposition affected the surface in a way to cause heterogeneous decomposition of tetraethyllead. Tetraethyllead at an initial pressure of 45.7 mm. was decomposed at 275.0° and the rate constant found was 22.8×10^{-4} sec.$^{-1}$. This is the value found in Part I.

The results of the experiments with azomethane and ethyl radicals were calculated as outlined above. From the initial reading of the pressure of tetraethyllead and from the time of that reading, the pressure at zero time was calculated. Similarly, the partial pressure of the tetraethyllead and its products was calculated for the time of the introduction of the azomethane. From the observed total pressure at this time, that of the azomethane was obtained by difference. The partial pressure of the azomethane and its products was calculated for each subsequent reading from the rate constants reported by Ramsperger,[4] and this was subtracted from the total. The resulting pressures were used to calculate first order rate constants for the decomposition of the tetraethyllead. In the latter calculations the ratio of final to initial pressure was assumed to be 2.00 for 275.0° and 2.19 for 260.0°. Table III gives the data of a sample experiment.

TABLE III

DATA FOR SAMPLE EXPERIMENT ON AZOMETHANE AND ETHYL RADICALS

Expt. 19; $T = 275.0°$; $P_{\text{initial, Tet.}} = 30.7$ mm. (calcd.); $P_{\text{final, Tet.}} = 61.7$ mm. (obs.); $P_{\text{final, Tet.}} = 61.4$ mm. (calcd.); $P_{\text{final}}/P_{\text{initial}} = 2.01$; $P_{\text{initial, Azo.}} = 45.9$ mm. (obs.); $P_{\text{initial, Azo.}}/P_{\text{initial, Tet.}} = 1.50$.

P_{Total}	P_{Azo}	$P_{\text{T, P}}$	$P_{\text{Tet.}}$	t, sec.	$k_1 \times 10^4$, sec.$^{-1}$
35.1	0	35.1		73	
84.0	45.9	38.1 (cal.)		130	
87.3	45.9	41.4	20.0	182	
91.6	45.9	45.7	15.7	297	20.9
94.9	46.1	48.8	12.6	403	20.6
97.9	46.3	51.6	9.8	530	19.9
104.4	47.4	57.0	4.4	909	21.1
111.5	49.8	61.7	0	2455	

The pressures in columns 1, 2, 3 and 4 are in mm. The first column gives the observed total and the second column lists the calculated partial pressures of azomethane. Column three gives the partial pressures of the tetraethyllead and its decomposition products; column four, those of the tetraethyllead. Table IV is a summary of all the experiments.

TABLE IV

SUMMARY OF ALL EXPERIMENTS ON AZOMETHANE AND ETHYL RADICALS

No.	Temp., °C.	$P_{\text{Tot.}}$, mm.	$P_{\text{Azo.}}$, mm.	$P_{\text{Azo.}}/P_{\text{Tot.}}$	$(P_{\text{init.}}/P_{\text{fin.}})_{\text{Tet.}}$	$k_1 \times 10^4$
19	275.0	30.7	45.9	1.50	2.01	20.6
20		36.8	66.9	1.82	2.02	20.2
21		28.6	97.5	3.41		24.4
6–10		19–53	0	0	2.00	22.0
22	260.0	29.1	69.7	3.08		6.00
23		36.8	90.8	2.46		6.52
1–4		13–44	0	0	2.19	8.47

The column headings are self-explanatory. Experiments listed as numbers 6–10 and 1–4 are taken from Part I of this paper. Each of the other experiments was carried out with a higher pressure of azomethane than of tetraethyllead in order to provide favorable conditions for reaction of the ethyl radicals with azomethane.

Discussion of Results.—It is seen from Table IV that the first order rate constants calculated for the decomposition of tetraethyllead in the presence of azomethane are the same, at 275.0°, as those found in Part I. At 260.0° the constants of Part I are about 25% greater than those found here. At neither temperature are the calculated rates greater when azomethane is present. This fact is considered to be strong evidence that in the system here investigated there is no reaction between azomethane and ethyl radicals. The agreement of the final–initial pressure ratios found in experiments 19 and 20 with those found in experiments 6–10 is equally convincing evidence of this lack of reaction. The reason for the 25% drop in rate constant found in experiments 22 and 23 is not obvious. The more interesting observation for the present problem is that the rate is not increased over that found in numbers 1–4.

III. Hydrogen and Ethyl Radicals

Von Hartel and Polanyi[11] have found that methyl radicals react with hydrogen at temperatures above 300°. They calculate for the reaction $CH_3 + H_2 = CH_4 + H$ an activation energy of 8 kilocalories. Simons, McNamee and Hurd[12] argue from certain qualitative observations that there must be some reaction of hydrogen with methyl radicals, even at room temperature. Their arguments may be extended to apply to ethyl radicals, since Paneth and co-workers have shown methyl and ethyl radicals to behave very much alike. Geddes and Mack[7] made experiments at 442° on the decomposition of germanium tetraethyl in the presence of hydrogen; they concluded that there was some reaction of the hydrogen with the germanium alkyl or with its decomposition products. Since they found approximately the same rate of decomposition of the germanium tetraethyl in the presence of hydrogen as in its absence, it must be concluded that the reaction probably occurs with the products of the decomposition. This points to a reaction of hydrogen with ethyl radicals at 442°. In order to determine if hydrogen reacts with ethyl radicals at temperatures around 275°, several experiments were performed with hydrogen in the same manner as those carried out with azomethane.

Materials, Apparatus and Procedure.—The hydrogen used was commercial tank hydrogen. The tetraethyllead was the same as in Parts I and II. The apparatus was the same as in Part II except that stopcock H in Fig. 1 led to a 2-liter flask filled with hydrogen. The procedure was identical with that in Part II, hydrogen being substituted for azomethane.

Experimental Results.—The calculations were made in the same manner as described in Part II except that it was not necessary to compute the pressures of hydrogen for each of the readings. The hydrogen pressure was assumed to remain constant and to have the value determined at the start of the run. All of the experiments were allowed to continue until the tetraethyllead was completely decomposed, and final–initial pressure ratios for the decomposition were calculated. Table V is a summary of all the runs.

The column headings have the significance they have in Table IV.

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(11) Von Hartel and Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

(12) Simons, McNamee and Hurd, *J. Phys. Chem*, **36**, 946 (1932).

TABLE V

SUMMARY OF ALL EXPERIMENTS ON HYDROGEN AND ETHYL RADICALS

No.	Temp., °C.	$P_{\text{Tet.}}$, mm.	P_{H_2}, mm.	$P_{H_2}/P_{\text{Tet.}}$	$(P_{\text{init.}}/P_{\text{fin.}})_{\text{Tet.}}$	$k_1 \times 10^4$
26	275.0	25.1	108.4	4.32	1.98	27.5
27		26.1	132.9	5.09	2.03	26.1
28		39.3	84.0	2.14	1.94	24.7
6–10		19–53	0	0	2.00	22.0
29	260.0	31.7	114.5	3.61	2.10	9.8
30		39.4	80.3	2.04	2.07	9.6
1–4		13–44	0	0	2.19	8.5

Discussion of the Results.—The most significant results of the experiments listed in Table V are the final–initial pressure ratios. At 275.0° these are the same, within the limits of error, for the experiments made with and without hydrogen. The ratios for the experiments at 260.0° in which hydrogen was present are slightly lower than those in experiments 1–4; the difference is not sufficiently great to be certain that it is real. The 15% increase in rate above that found in Part I, as shown in column 7, is more or less incompatible with the agreement shown in column 6. The discrepancy is very probably due to the presence of small amounts of oxygen in the hydrogen. Geddes and Mack[7] found that traces of oxygen markedly accelerated the rate of decomposition of germanium tetraethyl; it is likely that oxygen has the same effect on the decomposition of tetraethyllead. It should be pointed out that any reaction of ethyl radicals with hydrogen would cause a lowering of the rate constants as calculated here; this is due to the fact that the pressure increase would be less than that expected from the tetraethyllead decomposition alone.

Because of the sensitivity of the rate of decomposition of tetraethyllead to oxygen, less emphasis should be placed upon the constants of column 7 than upon the final–initial pressure ratios; this is particularly true because the presence of slight traces of oxygen would affect the latter very little. If all of the ethyl radicals reacted with hydrogen according to the equation $4C_2H_5 + 2H_2 = 4C_2H_6$ the ratio of final to initial pressure would be 4 to 3, or 1.33. Any reaction of hydrogen with ethyl radicals would thus lower the final–initial pressure ratio, the limiting value being 1.33. The results indicate that there is very little, if any, reaction of ethyl radicals with hydrogen in the system here investigated.

Conclusions

The experiments reported in Part II lead to the conclusion that in the system here investigated and at temperatures around 275° there is no reaction of ethyl radicals with azomethane. It would seem possible that the absence of this reaction could be due to a preferential reaction of the radicals with the undecomposed tetraethyllead. Meinert[8] obtained good evidence that in a system very similar to that used here the reaction of ethyl radicals with tetraethyllead was a wall reaction. If this is so, before diffusion of the radicals to the walls there must occur quite a large number of collisions between the radicals and the azomethane present in the reaction vessel. This indicates that the absence of a homogeneous reaction between ethyl radicals and azomethane is not due to a preferential reaction of the radicals with the lead alkyl; it must be concluded that the inertia is due to the comparatively high activation energy associated with the reaction.

It is quite probable that there would be no reaction of methyl radicals with azomethane under conditions identical with those employed for the investigation with ethyl radicals. If this is true, since the experiments on the decomposition of azomethane have been performed in reaction systems quite similar to that used here, we may conclude that there are no short reaction chains involving methyl radicals which accompany the unimolecular decomposition of azomethane as measured by Ramsperger.[4]

The results of Part III indicate that there is very little, if any, reaction of hydrogen with ethyl radicals at temperatures in the neighborhood of 275°.

Paneth and Lautsch[13] have measured the half-lives of ethyl radicals under various conditions. From their results we may conclude that an ethyl radical would retain its identity in the reaction system employed here for at least 10^{-3} sec. In 10^{-3} sec. an ethyl radical would collide about 10^7 times at 275° with hydrogen (or azomethane) which was at a partial pressure of 100 mm. From our experimental results the fraction of effective collisions must be smaller than 10^{-7}. Therefore, the activation energy of a bimolecular reaction between ethyl radicals and hydrogen or azomethane is calculated to be greater than 15 kilocalories.

I wish to thank Professor G. B. Kistiakowsky for the advice and help which have aided in this research.

Summary

1. The kinetics of the thermal decomposition of tetraethyllead have been studied at temperatures of 245.0, 260 and 275.0° and from initial pressures of 13 to 52 mm. The decomposition was found to be unimolecular and between 96 and 97% homogeneous. The rate constants measured in the system here used are quite well given by the equation $k_1 = 1.2 \times 10^{12} e^{-36,900/RT}$ sec.$^{-1}$.

2. Ethyl radicals were found not to react with azomethane at temperatures around 275°. It is concluded that there are no chains accompanying the unimolecular decomposition of azomethane.

3. Ethyl radicals were found to react very little, if any, with hydrogen at 275°.

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(13) Paneth and Lautsch, *Ber.*, **64**, 2708 (1931).

4. The activation energies of bimolecular reactions of ethyl radicals with hydrogen or azomethane are calculated to be greater than 15 kilocalories.

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The Dissociation of Water in Lithium Bromide Solutions at 25°

BY JOHN E. VANCE

The dissociation of water has been determined by means of electromotive force measurements in several salt solutions. A complete list of references on the subject and a discussion of the method is available.[1]

To afford a comparison with lithium chloride a similar determination in lithium bromide solutions has been undertaken.

The electromotive forces of the cells $H_2 \mid LiOH(m_1), LiBr(m_2) \mid AgBr \mid Ag$ are connected with the desired function through the equation

$$\log K_\gamma = \log \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} = \frac{E - E_0 + 0.05915 \log m_2/m_1}{0.05915} + \log K_w + \log \gamma_H\gamma_{Br} \qquad (1)$$

where K_w is the equilibrium constant for the dissociation of water.

By measuring the above cell with a constant value of m_1 and several values of m_2, and by determining $\gamma_H\gamma_{Br}$ $(m = 0)$ in lithium bromide solutions of the same total ionic strength, we can evaluate K_γ if we know E_0 and K_w in pure water. E_0 has recently been determined to be 0.07172 v.,[2] and K_w has been found by electromotive force measurements to be 1.008×10^{-14}.[3] The associated functions $m_w = m_H = m_{OH}$, $\gamma_H\gamma_{OH}$, and $\gamma = \sqrt{\gamma_H\gamma_{OH}}$ can then be calculated if a_{H_2O} is obtainable.

Measurement of the Cells: $H_2 \mid LiOH(m_1), LiBr(m_2) \mid AgBr \mid Ag$.—The determinations were carried out in the usual type of cell. The silver bromide electrodes were protected from light and carbon dioxide was carefully excluded from the cells and solutions. Table I gives the results; column six the mean electromotive force.

In equation (3), rearranged to give

$$E - E_0 + 0.05915 \log m_2/m_1 = -0.05915 \log K_w\, a_{H_2O} - 0.05915 \log (\gamma_H\gamma_{Br}/\gamma_H\gamma_{OH}) \qquad (1a)$$

it is seen that by plotting the left side against μ the function will extrapolate to 0.05915 log K_w at infinite dilution. Use was made of this equation to obtain values of E at round concentrations. Column seven of Table I gives the value of the left side of equation (1a) as determined and column two of Table III gives the value at round concentrations.

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(1) Vance, THIS JOURNAL, 55, 2729 (1933); Harned and Mason, *ibid.*, 54, 3112 (1932).

(2) Harned and Hamer, *ibid.*, 55, 4496 (1933).

(3) (a) Harned and Copson, *ibid.*, 55, 2206 (1933); (b) Harned and Hamer, *ibid.*, 55, 2194 (1933).

TABLE I

THE ELECTROMOTIVE FORCES OF THE CELLS: H_2 | LiOH (m_1), LiBr (m_2) | AgBr | Ag

m_1	m_2	μ	No. of cells	Δ(m. v.)	E	$[E - E_0 + 0.05915 \log m_1/m_2]$
0.009913	0.02002	0.02993	2	0.21	0.8801	0.8264
.009963	.04999	.05995	2	.20	.8563	.8260
.009990	.07479	.08478	2	.02	.8451	.8251
.009995	.09995	.1099	2	.32	.8372	.8246
.009969	.1976	.2076	2	.12	.8182	.8232
.009991	.3016	.3116	2	.18	.8058	.8216
.009973	.4020	.4120	2	.07	.7968	.8200
.009985	.4994	.5094	2	.15	.7900	.8188
.009908	.7480	.7579	2	.27	.7761	.8155
.01000	1.0007	1.0107	2	.07	.7651	.8117
.01000	1.4993	1.5093	2	.34	.7486	.8056

The Determination of the Activity Coefficient of Hydrobromic Acid in Lithium Bromide Solutions.—The cell H_2|HBr (0.01), LiBr(m)|AgBr|Ag was measured, and the electromotive forces so obtained were subtracted from the electromotive force of the cell: H_2 | HBr(0.01) | AgBr | Ag.

This process is equivalent to the direct measurement of the cell: Ag | AgBr | HBr(0.01), LiBr (m) | H_2 | HBr (0.01) | AgBr | Ag. The equation connecting the electromotive force of the last cell with the activity coefficient of the acid is

$$E = 0.1183 \log \frac{\gamma_{\mathrm{HBr}}}{0.906} \left[\frac{(0.01 + m)}{0.01}\right]^{1/2} \tag{2}$$

where 0.906 is the activity coefficient of hydrobromic acid at a concentration of 0.01 m in its own solution. Values of $\gamma_{\mathrm{HBr}\,(0.01)}$ at round concentrations were obtained by plotting the values of $\gamma_{\mathrm{HBr}\,(0.01)}$ from equation (4) against $\mu^{1/2}$. Values of $\gamma_{\mathrm{H}}\gamma_{\mathrm{Br}\,(0.0)}$ are required by equations (1) and (1a), and can be found by making the usual short extrapolation of

TABLE II

THE ACTIVITY COEFFICIENT OF 0.01 MOLAL HYDROBROMIC ACID IN LITHIUM BROMIDE SOLUTIONS AT 25°

m	No. of cells	Δ(m. v.)	E	$\gamma_{\mathrm{HBr}\,(0.01)}$	m	No. of cells	Δ(m. v.)	E	$\gamma_{\mathrm{HBr}\,(0.01)}$
0.0	15	0.2	0.31343	0.906	0.7993	1	...	0.20488	0.833
.02500	3	.04	.28401	.859	.8997	1	...	.20089	.849
.04827	1	...	.27263	.830	.9010	1	...	.20058	.854
.07472	1	...	.26406	.814	.9996	2	0.0	.19720	.866
.1004	2	0.15	.25769	.806	1.1989	1	...	.19041	.903
.1994	1	...	.24270	.784	1.4008	1	...	.18354	.956
.2995	1	...	.23324	.776	1.5996	1	...	.17724	1.011
.4016	2	0.1	.22561	.780	1.7893	1	...	.17133	1.074
.5016	1	...	.21940	.790	1.9837	1	...	.16541	1.144
.5993	1	...	.21458	.795	2.2502	1	...	.15851	1.229
.6002	1	...	.21432	.798	2.2581	1	...	.15813	1.236
.7006	1	...	.20936	.815	2.4893	1	...	.15137	1.343

$\gamma_{HBr\ (0.01)}$,[4] to obtain $\gamma_{HBr\ (0.0)}$ and then by squaring $\gamma_{HBr\ (0.0)}$. Table II contains the values of the measured electromotive forces and of $\gamma_{HBr\ (0.01)}$. Column three of Table III gives the values of $\gamma_{HBr\ (0.01)}$ at round concentrations and column four the corresponding values of $\gamma_H\gamma_{Br\ (0.0)}$.

The Calculation of a_{H_2O} in Lithium Bromide Solutions.—Values of a_{H_2O} in these solutions were calculated from the activity coefficients of lithium bromide according to the method originated by Harned.[5] The values of γ_{LiBr} used were those given by Harned.[6] The activity coefficients of lithium bromide can be expressed by the equation

$$\log \gamma_{LiBr} = -\beta m\alpha' + \alpha m \tag{3}$$

when the constants have the values $\beta = 0.271$, $\alpha' = 0.361$ and $\alpha = 0.177$. Values of a_{H_2O} were subsequently calculated from the equation

$$\ln \frac{1}{a_{H_2O}} = \frac{m}{55.5}\left[\nu + \frac{2.303\ \alpha\nu m}{2} - \frac{2.303\ \beta\nu\alpha'}{\alpha' + 1}\ m^{\alpha'}\right] \tag{4}$$

These values are given in column six of Table III.

TABLE III

CALCULATION OF K_γ FROM DATA IN TABLES I AND II, WITH VALUES OF m_w, $\gamma_H\gamma_{OH}$ AND $\sqrt{\gamma_H\gamma_{OH}}$ AT ROUND CONCENTRATIONS

μ	$[E - E_0 + 0.05915 \log m_2/m_1]$	$\gamma_{HBr\ (0.01)}$	$\gamma_H\gamma_{Br\ (m=0)}$	K_γ	a_{H_2O}	$m_w \times 10^7$	$\gamma_H\gamma_{OH}$	γ
0.03	0.8267	0.865	0.747	0.712	0.999	1.19	0.711	0.844
.04	.8263	.851	.723	.679	.999	1.22	.678	.824
.05	.8261	.840	.702	.655	.998	1.24	.654	.809
.06	.8258	.830	.685	.632	.998	1.26	.631	.794
.075	.8254	.820	.669	.608	.997	1.29	.606	.779
.10	.8249	.808	.650	.579	.997	1.32	.577	.760
.15	.8240	.790	.621	.534	.995	1.37	.531	.729
.20	.8232	.780	.605	.504	.993	1.41	.500	.708
.40	.8202	.772	.593	.440	.986	1.51	.434	.659
.60	.8174	.798	.632	.420	.978	1.55	.411	.641
.80	.8147	.826	.679	.406	.971	1.58	.394	.627
1.00	.8120	.863	.740	.398	.963	1.59	.383	.619
1.25	.8088	.914	.830	.394	.952	1.60	.375	.612
1.50	.8057	.978	.950	.401	.942	1.59	.378	.615

Calculation of K_γ, m_w, $\gamma_H\gamma_{OH}$ and γ.—These functions can now be calculated from equation (1). The values of K_γ, m_w, $\gamma_H\gamma_{OH}$ and $\gamma = \sqrt{\gamma_H\gamma_{OH}}$ are given in columns five, seven, eight and nine, respectively, of Table III. The values for K_γ in these solutions are slightly but definitely lower than the values found in lithium chloride solutions.[3a]

Summary

1. The electromotive forces of the cells: H_2 | LiOH (m_1), LiBr (m_2) | AgBr | Ag, and of the cells: H_2 | LiBr (m), HBr (0.01) | AgBr | Ag, have

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(4) See, for example, Harned and Mason, THIS JOURNAL, 54, 3112 (1932).

(5) See Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1924, first edition, Vol. II, pp. 751–753.

(6) Harned, THIS JOURNAL, 51, 416 (1929).

been measured and the activity coefficient of 0.01 *m* hydrobromic acid determined in lithium bromide solutions.

2. From a combination of the data obtained from the two cells and from the known activity coefficients of lithium bromide, the dissociation of water in lithium bromide solutions has been calculated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Further Discussion of the Surface Tension of Film-Covered Liquids at Saturation

BY HENRY BROWN

The surface tension[1] σ_{13} registered at saturation vapor pressures by a liquid covered with a film is given by

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \tag{1}$$

This equation must be interpreted differently for a film of monomolecular thickness from that for a film of such thickness that its interior possesses the properties of a phase in mass. In the latter case, two surfaces of discontinuity exist, and hence two surface tensions σ_{12} and σ_{23}, but in the former case the value σ_{13} cannot be interpreted in terms of σ_{12} and σ_{23}, *per se*. The lowering of the surface tension of the liquid by the molecules of the monomolecular film is to be explained by the closer packing of the film molecules as a two-dimensional phase[2] according to the familiar conceptions developed by Langmuir.

The amount of lowering of the surface tension by a given number of film molecules when packed in the form of a monomolecular film would be different from that when packed as a polymolecular film of the same area, and since in the former case all the film molecules would be in closer contact (in fact, they would be in direct contact) with the molecules of the supporting liquid, it follows that the monomolecular film would cause the greater lowering of the surface tension for the same number of molecules per unit area, *i. e.*, for the same value of the film density; hence the monomolecular film is of greater stability, and by condensation from the vapor probably never becomes a thicker film with an interior having,

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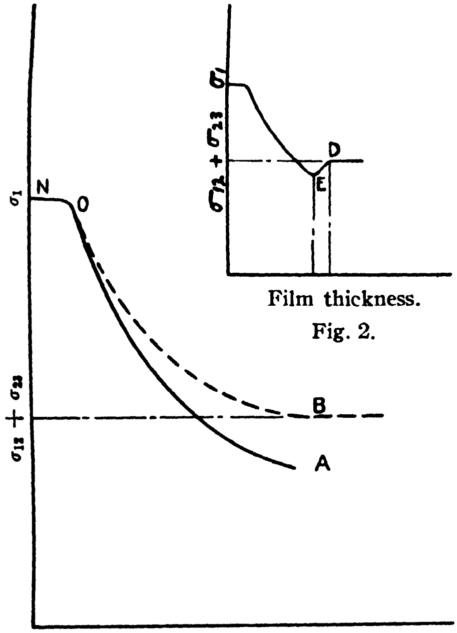
(1) Bartell, Case and Brown, THIS JOURNAL, 55, 2769 (1933).

(2) For a two-dimensional phase, the fundamental thermodynamic equation would be

$$d\epsilon = t\,d\eta - f\,ds + \mu_1 dm_1 + \mu_2 dm_2 + \dots \tag{2}$$

where in place of the $-p\,dv$ term of a three-dimensional phase (J. Willard Gibbs, equation 86), we have $-f\,ds$; the f is the two-dimensional outward pressure exerted by the molecules of the film in the plane of the film. The monomolecular film is to be considered as a part of the surface of discontinuity of the liquid, the fundamental equation of which (Gibbs, equation 501) contains a $+\sigma ds$ term instead of the $-f\,ds$ term above. These terms differ in sign because the natural tendency (to minimum potential energy) for the monomolecular film is to *expand* in area, whereas, for the surface of a liquid, to *contract*. It follows that the greater the value of f of the monomolecular film, the lower will be the value of σ.

at saturation, the properties of a phase in mass. But if we *start* with a thick film, then it would be unstable with respect to a finite variation, and upon a small disturbance would break up into a monomolecular film of lowered surface tension with the excess film liquid gathered in the form of lenses. This is illustrated by the curves given in Fig. 1, the ordinates of which denote surface tension values, and the abscissas the film densities, expressed, for example, in molecules per unit area. The curve NOA represents (in a general way) the case for films which always remain monomolecular in thickness, and the curve NOB (the curves may start curving concavely downward immediately from N instead of O) represents the case for films that gradually increase in thickness until at saturation vapor pressures the interior of the film attains the properties of a phase in mass. The authors[3] who have dealt with the problem of lens formation on film-covered surfaces have given a curve of the type shown in Fig. 2 (inset), which shows the relation of the surface tension values to *film thicknesses*, and it was necessary, in the explanation of the phenomena of the instability of thick films and lens formation, that the curve based on such coördinates possess a minimum in order to show the region of instability, the region indicated by DE. If, however, the true curve is the one for a film that always remains monomolecular in thickness, and the experimental evidence[4] is (unlike that for polymolecular films[5]) very conclusive for this, then by using the density of the film, or the area occupied per molecule, instead of the indefinite and for the case of



Film thickness.
Fig. 2.

Film density (molecules/(sq. cm.)

Fig. 1.—General relationship of surface tension to film density; curve NOA for a monomolecular film, NOB for a polymolecular.

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(3) Hardy, *Proc. Roy. Soc.* (London), **A86**, 610 (1912); **88**, 313 (1913); Bouasse, "Capillarité," Librairie Delagrave, Paris, 1924, pp. 356–360.

(4) Adam, "Physics and Chemistry of Surfaces," Oxford University Press, 1930, p. 29; Bouhet, *Ann. Phys.*, [10] **15**, 5 (1931).

(5) Cassel [*Trans. Faraday Soc.*, **28**, 177 (1932)] has obtained evidence that the film of carbon tetrachloride molecules adsorbed on the surface of mercury, attains at the saturated vapor pressure a density 3.6 times that of carbon tetrachloride in bulk, and because of the symmetry of this molecule, this result for a film thickness would represent the most accurate yet obtained for plane surfaces by calculation from surface tension lowering, were it not for the possible formation of capillary-active impurities by the contact of the organic halogen compound with mercury. This would cause the result to appear higher than the true value.

monomolecular films, erroneous coördinate, of film thickness, a curve without such a minimum is obtained, which is in accord with experimental facts. Moreover, a discontinuity will exist *between* the true curve NOA, and the curve NOB, given by a thick film. On the basis of this discontinuity, the instability of thick films and the formation of lenses on the film-covered surface are more logically illustrated in accordance with the existence of monomolecular films at saturation, as shown by the fundamental work of Devaux and Langmuir.

As indicated in Fig. 1, the value of σ_{13} equal to $\sigma_{12} + \sigma_{23}$ is a limiting value for a thick film, and this, as shown in the fundamental work of Hardy,[3] is not in accord with the phenomena of lens formation by spreading liquids. But monomolecular films are strictly in accord with the phenomena, since the value of σ_{13} equivalent to that given by $\sigma_{12} + \sigma_{23}$ is not a limiting value; instead, it represents merely a point on the surface tension–film density curve, for with further increase in the number of molecules per square cm. of film, σ_{13} falls to a lower value, and when it does, a lens of the liquid constituting the film can exist in equilibrium with the film. But the formation of lenses indicates a condition of supersaturation, and if we consider the film being formed by condensation from the saturated vapor under isothermal conditions, no lenses would appear on the film-covered surface; that is, the surface tension σ_{13} registers the value equal to $\sigma_{12} + \sigma_{23}$ at saturation vapor pressures. If σ_{13} falls lower than the value of $\sigma_{12} + \sigma_{23}$, the density of the monomolecular film, *i. e.*, the number of molecules per square cm. of film, must become greater than when $\sigma_{13} = \sigma_{12} + \sigma_{23}$, which means that the vapor pressure will also be greater; greater, that is, than for the film liquid in bulk (since the film liquid in the form of a film in bulk would also register the tension given by equation (1) above), and it is under these supersaturated conditions that a convex lens, or a dew of lenses, of the film liquid can exist in equilibrium with the film.

Summary

The surface tension value $\sigma_{13} = \sigma_{12} + \sigma_{23}$ registered at saturation vapor pressures by a liquid covered with a film is discussed for films of monomolecular and polymolecular thickness; the significance of the equation for the surface tension at saturation being very different for the two types of films.

ANN ARBOR, MICHIGAN

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Notes

Use of Amyl Alcohol in the Sodium Diethyl Dithiocarbamate Method for Estimation of Copper

BY R. W. THATCHER

Several laboratory workers have experienced some difficulty in securing a sharp separation of the amyl alcohol layer in using the McFarlane[1] method for the determination of copper in organic tissues.

I have found that if isoamyl alcohol (redistilled at 129–131°) is used, this difficulty is avoided and a sharp separation occurs in a very short time even after quite vigorous shaking of the mixture. The amyl alcohol layer is so clear that it is rarely necessary to filter it through paper to remove traces of water before final colorimetric comparison. On the other hand, if normal amyl alcohol (boiling point 138–140°) is used, the separation is slow and the alcohol layer often turbid. This difference is probably due to the greater solubility of normal amyl alcohol in water than that of the iso form.

[1] McFarlane, *Biochem. J.*, **26**, 1022 (1932).

DEPARTMENT OF CHEMISTRY
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The System Lead Acetate–Acetic Acid

BY ARTHUR W. DAVIDSON AND WILBERT CHAPPELL

The recent discovery by Tarbutton and Vosburgh[1] of a solvate of the composition $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$, stable at 25° in contact with lead acetate–acetic acid solutions containing small concentrations of water, made it seem probable that the lower portions of both branches of the previously presented freezing-point curve for the anhydrous binary system[2] corresponded to equilibria metastable with respect to this solvate. A reëxamination of the binary system was therefore undertaken, with the aid of crystals of the solvate kindly furnished by Dr. Vosburgh.

Pure acetic acid (m. p. 16.62°) was prepared as described in previous papers. Anhydrous lead acetate was made by recrystallizing the trihydrate twice from solution in dilute acetic acid, heating it to 125° for two days, moistening the slightly basic product with anhydrous acetic acid and heating again to 115° for six hours. The resulting substance melted at 204°, and on analysis for lead gave 63.81%, as compared with the calculated 63.71%. The synthetic method described in previous papers was employed, except that solutions of the appropriate concentrations were seeded with minute amounts of the plate-like crystals of the solvate before determining the freezing points. It is remarkable that, although this compound proved to be the stable solid phase throughout a long range of concentrations (12.0 to 36.5 mole per cent. of lead acetate), we have not observed a single instance of its spontaneous separation, without seeding, from anhydrous solutions.[3]

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[1] Tarbutton and Vosburgh, THIS JOURNAL, **54**, 4537 (1932).

[2] Davidson and McAllister, *ibid.*, **52**, 507 (1930).

The composition of the solid separating, on seeding, from saturated solutions in this range was determined by filtering it off, drying between porous tiles in a desiccator over sodium hydroxide for twenty hours, and analyzing for lead by means of precipitation as lead sulfate. Three analyses gave a mean value of 66.78 mole per cent. of lead acetate, proving it to be the hemisolvate, $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$.

The new freezing point data are tabulated below, and are shown, together with portions of the curves for acetic acid and unsolvated lead acetate as solid phases, in Fig. 1.

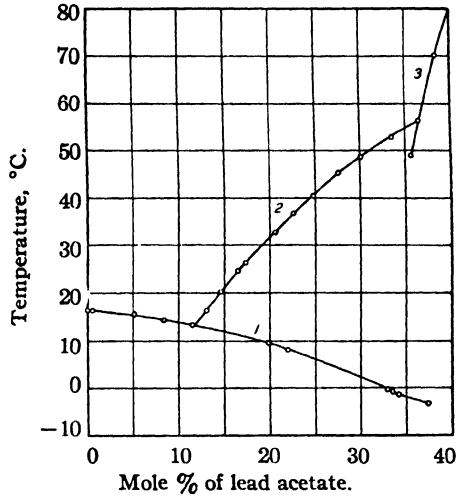

Fig. 1.—System $Pb(C_2H_3O_2)_2$–$HC_2H_3O_2$: 1, $HC_2H_3O_2$ as solid phase; 2, $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$ as solid phase; 3, $Pb(C_2H_3O_2)_2$ as solid phase.

$Pb(C_2H_3O_2)_2$, mole %	13.06	14.67	16.55	17.37	20.57	
Temperature, °C.	16.4	20.3	24.5	26.4	32.8	
$Pb(C_2H_3O_2)_2$, mole %	22.60	24.77	27.60	30.23	33.55	36.60
Temperature, °C.	36.7	40.5	45.2	48.7	52.9	56.4

The solubility of the hemisolvate at 25° is 3.35 moles per 1000 g. of solvent, 16.75 mole per cent. or 52.16 weight per cent. This value agrees well with the trend of the solubility data of Tarbutton and Vosburgh for solutions containing small amounts of water. At 56° the compound undergoes transition to unsolvated lead acetate.

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(3) *Cf.* Ref. 1, p. 4542.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Researches on Chlorimines. IV. A Study of the Reactions of Certain Ald-chlorimines with Bases

BY CHARLES R. HAUSER AND E. MOORE

The purpose of this paper is to report the results of a preliminary study of the reactions of aromatic ald-chlorimines with bases leading to the formation of nitriles (1). This reaction evidently does not consist of the spontaneous decomposition of ald-chlorimines (2), followed by the neutralization of the hydrogen chloride that would be produced, for certain ald-chlorimines which are relatively stable react more rapidly with a base than do certain others which are thermally unstable.[1] Moreover, the rate of decomposition of an ald-chlorimine is greatly accelerated by alkali, although the reaction apparently is not reversible.[2] Hence, the base is an active agent in removing the hydrogen chloride.

$$\mathrm{RCH{=}NCl + B \longrightarrow RCN + B{\cdot}H^+ + Cl^-} \qquad (1)$$

$$\mathrm{RCH{=}NCl \longrightarrow RCN + HCl} \qquad (2)$$

It should be of interest to determine the relative ease of removal of hydrogen chloride from ald-chlorimines by bases, since there is a possibility of correlating these data with the ionization constants of the corresponding acids and phenols. For this work we have chosen *o*-nitro-, *m*-nitro, *p*-chloro- and *p*-methoxy-benzalchlorimines, as they were readily available, and because their corresponding acids and phenols possessed ionization constants which differed from one another to an appreciable degree. Their relative rates of reaction have been determined with alkali in 95.6% alcohol, and with isoamylamine in benzene solution. Also, we have determined the relative rates of reaction of five different bases with *m*-nitrobenzalchlorimine in benzene solution.

Experimental

Solvents and Reagents.—Kahlbaum benzene was dried for a week over phosphorus pentoxide and then carefully fractionated through a 1.8-meter column. The middle fraction boiling at 79.9 ± 0.1° was used.

Eastman isoamylamine was dried for a week over solid potassium hydroxide and then decanted and distilled through a four-bulb column. The middle fraction distilling at 96.6 ± 0.1° was used. Eastman piperidine, benzylamine, acetamide and triphenylamine were used without further purification. Alcoholic alkali solution (0.04 *M*) was prepared from sodium and 95.6% alcohol.

Ald-chlorimines.—The ald-chlorimines used in this work were prepared from the corresponding aldehydes and monochloramine and recrystallized from cold dilute alcohol by methods described previously.[1] The products were pressed on porous plates until essentially dry and then kept over potassium hydroxide in desiccators at 5° for several hours. Special care was taken to dry thoroughly the samples that were used in the work with benzene solutions. Certain of the chlorimines used in this work gave analytical figures for active chlorine which were practically identical with the theoretical values, and all of the products were at least 99% pure.

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(1) (a) Hauser, Hauser and Gillaspie, THIS JOURNAL, **52**, 4163 (1930); (b) Hauser and Gillaspie, *ibid.*, **52**, 4518 (1930).

(2) Nitriles add hydrogen chloride to form imido chlorides (RCCl=NH) or nitrile hydrochlorides (RCN·HCl), Hantzsch, *Ber.*, **64B**, 667 (1931); see also Stephen, *J. Chem. Soc.*, **127**, 1874 (1925). Mr. A. E. Rainsford has shown in this Laboratory that when hydrochloric acid is added to an alcoholic solution of *p*-chlorobenzonitrile in an atmosphere of carbon dioxide, no test for active chloride is obtained.

Reaction of Ald-chlorimines with Bases.—Previously,[1b] yields of nitriles as high as 96% of the theoretical quantities have been isolated from the reaction products of ald-chlorimines and alkali. When *p*-methoxybenzalchlorimine in alcoholic solution was decomposed by alkali, the product obtained after removing the alcohol and washing with water was practically pure nitrile (m. p. 57°). Tests for aldehydes were negative.

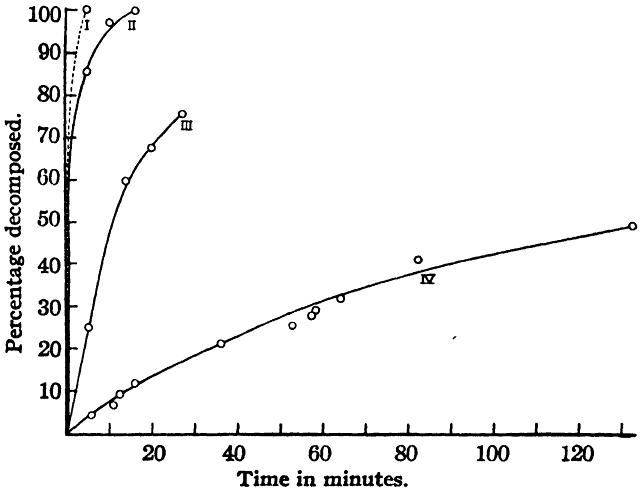

Fig. 1.—Relative rates of reaction of 0.01 *M* substituted benzalchlorimines with 0.02 *M* alkali in 95.6% alcoholic solution at 0°: I, *o*-nitro-; II, *m*-nitro-; III, *p*-chloro-; IV, *p*-methoxy-.

It has been shown in the following manner that ald-chlorimines neutralize equivalent molecular quantities of alkali. Alcoholic solutions of the chlorimines were mixed with excess of standard alkali. After tests for active chlorine were negative, the excess base was titrated with standard acid, using phenolphthalein as indicator. The data are given in Table I. The *o*- and *m*-nitrobenzalchlorimines were completely decomposed at 0° within a few minutes (see Fig. 1). Since the *p*-chloro and *p*-methoxy compounds were allowed to stand with the base at room temperature for several hours, blanks were run with the corresponding nitriles and alkali. The nitriles caused the neutralization of less than 2% of the alkali.

TABLE I

Calcd. 100 cc. 0.01 *M* o-$NO_2C_6H_4CH{=}NCl$ = 10.00 cc. 0.1 *N* NaOH. Found: 9.96 cc.
Calcd. 100 cc. 0.01 *M* m-$NO_2C_6H_4CH{=}NCl$ = 10.00 cc. 0.1 *N* NaOH. Found: 10.04 cc.
Calcd. 0.3046 g. p-$ClC_6H_4CH{=}NCl$ = 17.51 cc. 0.1 *N* NaOH. Found: 17.57 cc.
Calcd. 0.3172 g. p-$CH_3OC_6H_4CH{=}NCl$ = 18.71 cc. 0.1 *N* NaOH. Found: 18.68 cc.

It has been shown that ald-chlorimines react with amines in benzene solutions according to the equation $RCH{=}NCl + R'NH_2 \longrightarrow RCN + R'NH_2{\cdot}HCl$. The amine hydrochloride precipitated as white crystals from benzene solution in yields generally more than 90% of the theoretical quantities. After removing the excess amine by means of acid, the nitrile was obtained by evaporating the solvent. With *o*-nitrobenzalchlorimine and isoamylamine in benzene solution, a yield of nitrile corresponding to 90% of the theoretical quantity was obtained. However, with less reactive ald-chlorimines, impure products were obtained from which smaller yields of pure nitriles were isolated.

Rates of Reaction.—Equal volumes of 0.04 *M* alkali and 0.02 *M* ald-chlorimine solutions in 95.6% alcohol were mixed and kept at 0 ± 1°. At intervals samples were run into a mixture of acetic acid and potassium iodide solution, and titrated with standard thiosulfate, adding water near the end of the titration in order to obtain a starch–iodide end-point. It was shown that the ald-chlorimines were stable in neutral alcoholic solutions for several hours. In the general procedure for the reactions in benzene solution 5-cc. samples of 0.4 *M* amine and 0.2 *M* ald-chlorimine solutions were mixed in test-tubes and kept at 30 ± 0.1°. At intervals the contents of the tubes were shaken with a mixture of 5 cc. of acetic acid, 5 cc. of 50% potassium iodide solution and 10 cc. of alcohol and titrated with thiosulfate. Difficulty was encountered in these analyses of benzene solutions of the chlorimines. However, the results with isoamylamine could usually be checked within ±5% during the first half of the decompositions. The rate of decomposition of *m*-nitrobenzalchlorimine in 0.1 *M* benzene solution was measured as a blank.

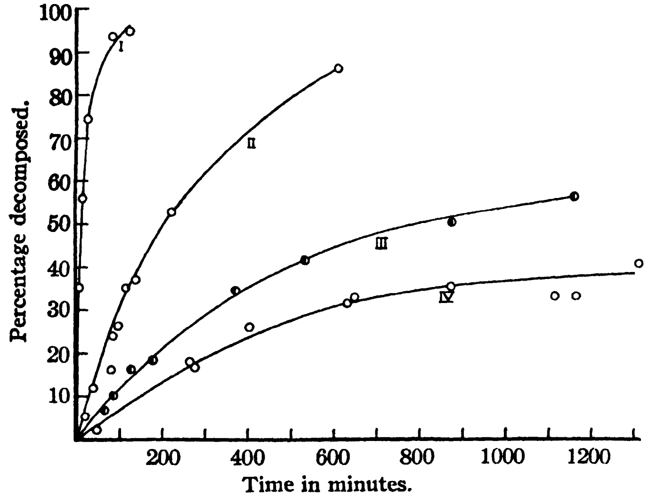

Fig. 2.—Relative rates of reaction of 0.1 *M* substituted benzalchlorimines with 0.2 *M* isoamylamine in benzene solutions at 30°: I, *o*-nitro-; II, *m*-nitro-; III, *p*-chloro-; IV, *p*-methoxy-.

The percentage chlorimine decomposed has been plotted against the corresponding time in Figs. 1, 2 and 3. In Fig. 3 the approximate ionization constants of the three strongest bases are also given. For comparison, the results for acetamide, triphenylamine and the blank are plotted on the same diagram using a different time scale. Their experimentally determined results can be obtained by multiplying the values given for the time by ten. Due to the limited solubility of acetamide in benzene its concentration was two-thirds that of the other bases. After periods of thirty and forty-five days the percentage decompositions of the blank were 25 and 50%, whereas those of the chlorimine in the presence of triphenylamine were 13 and 22%, respectively. Although the products of decomposition of the chlorimine evidently accelerated its further decomposition in both cases, the chlorimine was apparently more stable in the presence of the triphenylamine.

***p,p'*-Dichlorobenzophenone Chlorimine[3] with Bases.**—This keto-chlorimine was allowed to react with alkali in alcoholic solution, and with isoamylamine in benzene solution under conditions similar to those used in the work with ald-chlorimines described above. After periods of one and one-half and thirty hours the active chlorine content of an alcoholic solution of 0.01 *M* chlorimine with 0.02 *M* alkali at 0° was decreased to the extent of 0.5 and 3.5%, respectively. When the alcohol was evaporated on a water bath a product was obtained which was identified as *p,p'*-dichlorobenzophenone.

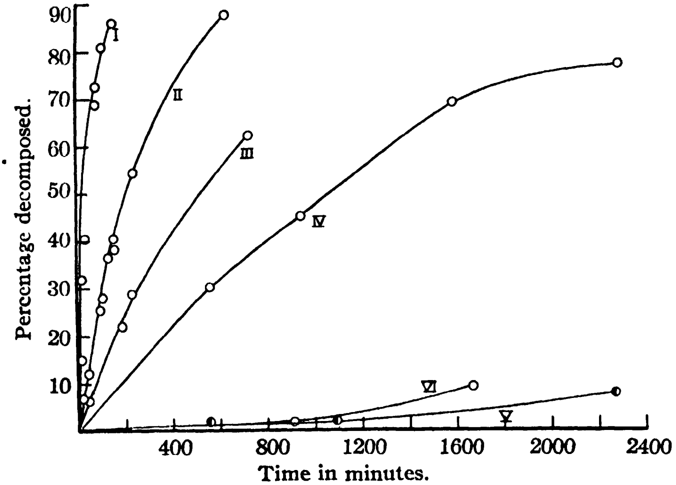

Fig. 3.—Relative rates of reaction of 0.2 *M* bases with *m*-nitrobenzalchlorimine in benzene solution at 30° : I, piperidine, $K_B = 1.3 \times 10^{-3}$; II, isoamylamine, $K_B = 4 \times 10^{-4}$; III, benzylamine, $K_B = 2 \times 10^{-5}$; IV, acetamide (multiply time scale by ten); V, blank (multiply time scale by ten); VI, triphenylamine (multiply time scale by ten).

The keto-chlorimine (0.1 *M*) with isoamylamine (0.2 *M*) in benzene solution at 30° was 2% decomposed after nineteen hours and 10% after six days.

TABLE II

IONIZATION CONSTANTS OF ACIDS, PHENOLS AND ANILINES CORRESPONDING TO SUBSTITUTED BENZALCHLORIMINES

Benzalchlorimines	*o*-Nitro-	*m*-Nitro-	*p*-Chloro-	*p*-Methoxy-
Acids K_A	6×10^{-3}	3×10^{-4}	9.1×10^{-5}	3.3×10^{-5}
Phenols K_A	5.6×10^{-8}	5×10^{-9}	4×10^{-10}	....
Anilines K_B	1.5×10^{-14}	3.2×10^{-12}	1.2×10^{-11}	5.7×10^{-9}

Discussion of Results

Evidence is presented in the experimental part which indicates that the reaction of 0.02 *M* alkali with 0.01 *M* ald-chlorimine[4] in alcoholic solution

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[3] Hauser and Humble, THIS JOURNAL, 54, 2476 (1932).

[4] Bimolecular constants calculated for 10 to 50% decomposition of *p*-methoxybenzalchlorimine agreed within ±5%. The average value was 0.285.

(Fig. 1) proceeded quantitatively according to equation (1). The predominant reaction of 0.2 *M* isoamylamine with 0.1 *M* ald-chlorimine in benzene solution (Fig. 2) also can be represented by equation (1). It is probable that the extent of side reaction which occurred under these conditions was less than 2% during the first half of the decompositions of the ald-chlorimines, since, in an interval of nineteen hours, *p,p'*-dichlorobenzophenone chlorimine was only 2% decomposed, whereas the corresponding ald-chlorimine was 55% decomposed under similar conditions. The results in Figs. 1, 2 and 3 are considered to represent merely the relative rates of reactions of these ald-chlorimines with bases.

It is evident from Figs. 1 and 2 and Table II that the relative ease of removal of hydrogen chloride from *o*-nitro-, *m*-nitro, *p*-chloro- and *p*-methoxy-benzalchlorimines by means of alkali in alcoholic solution, and by means of isoamylamine in benzene solution, is in the same relative order as the ionization constants of the corresponding acids and phenols, and in the inverse order to those of the corresponding substituted anilines. It can be seen from Fig. 3 that the relative rates of reaction of various amines with *m*-nitrobenzalchlorimine in benzene solution are in the same relative order as the ionization constants of the bases.[5]

The writers believe that the most plausible mechanism for the removal of hydrogen chloride consists of the withdrawal of a proton* from the ald-chlorimines ($RCH^*{=}NCl$) under the influence of the base, followed by the removal of the chloride ion. The fact that keto-chlorimines ($RCR{=}NCl$) do not react with bases in this manner indicates that the removal of the chloride ion from an ald-chlorimine to form a nitrile depends upon the presence of the aldehydic hydrogen. It is possible therefore to regard the relative rates of reaction of the various ald-chlorimines with a base as a measure of the relative reactivities of the aldehydic hydrogen of these ald-chlorimines.

Summary

It has been shown that the relative ease of removal of hydrogen chloride from *o*-nitro-, *m*-nitro-, *p*-chloro- and *p*-methoxy-benzalchlorimines by means of alkali in alcoholic solution, and by means of isoamylamine in benzene solution, are in the same relative order as the ionization constants of the corresponding acids and phenols. It was shown also that the relative rates of reaction of various amines with *m*-nitrobenzalchlorimine in benzene solution are in the same relative order as the ionization constants of the bases.

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(5) Since these ionization constants have been determined in water, only a qualitative relationship was expected between these constants and the rates of reaction of the bases with the ald-chlorimine in benzene solution. The rate for acetamide, however, was much faster than would be expected from its basic strength.

[CONTRIBUTION FROM THE LABORATORY FOR ORGANIC CHEMISTRY OF THE TECHNICAL HIGH SCHOOL, DELFT, HOLLAND]

The Diazotization of Very Weakly Basic Amines

BY H. A. J. SCHOUTISSEN

Measurements in relation to the velocity of the diazotization reaction with different quantities of hydrochloric acid[1] have led to the conclusion that this reaction proceeds between the *ammonium* salt and nitrous acid. Now the concentration of the amino salt in the solution is directly proportional to the degree of the basicity of the amine. In consequence of the researches published in a previous communication[2] it follows that the substituents in the benzene nucleus exert a twofold *opposing* influence on the velocity of the diazotization reaction: (1) *a diminution of the velocity* with the negativeness of the substituent in consequence of the reduced basicity of the amine, the basicity *decreasing* in the order: *meta, para, ortho;* (2) *an increase of velocity* as the substituent is more negative, in consequence of the influence of the group on the velocity of transposition of the ammonium group, the velocity *increasing* in the order: *meta, para, ortho.* If in consequence of the reduced basicity hydrolysis is so much advanced that no ammonium salt is present in the usual concentrations of mineral acid, no diazotization is to be expected. Theoretically this can be anticipated with very highly negative substituted amines. Instances of this kind are known in chemical literature. Trichloro-, tribromo- and 2,4-dinitroaniline, *e. g.*, are only diazotizable under conditions of highly increased concentrations of mineral acid. Also many cases are known in which even under these conditions diazotization is not successful.

An example of such an amine is picramide.

The advantage owing to sulfuric acid being a strong acid which can be employed in high concentrations is nullified by the fact that it combines with all the nitrous acid, as is proved by following experiments.

A solution of aniline in sulfuric acid (1.84) has been mixed during an hour with the theoretical quantity of nitrosylsulfuric acid; temp. 0°. Concentrated nitric acid (d. 1.51) is added in excess, temp. 0°. After two hours the reaction mixture is poured into a solution of potash and coupled with β-naphthol. The product of coupling existed in the main as *m*-nitrobenzene-azo-β-naphthol, m. p. 193°, and contained only a very small quantity of benzene-azo-β-naphthol, m. p. 133°. We may conclude therefore that the diazotization with nitrosylsulfuric acid does *not* take place or proceeds very slowly, *as otherwise the primarily formed diazonium compound will resist nitration.*[3]

Still more convincing evidence may be obtained in the following way.

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(1) Schoutissen, These Delft, Editors Nygh and v. Ditmar, Rotterdam.

(2) Böeseken, Brandsma and Schoutissen, *Proc. Royal Society, Amsterdam*, Feb. 28, 1920.

(3) Schoutissen, *Rec. trav. chim.*, **40**, 763 (1921).

p-Aminobenzaldehyde (2.5 g.) is dissolved in 30 cc. of concentrated sulfuric acid and mixed with 1.45 g. of sodium nitrite in 15 cc. of sulfuric acid (1.84) temp. 0°. After two hours nitrobenzene is added, *p*-aminobenzaldehyde precipitating. No diazotization has taken place.

Therefore the writer has tried to release the nitrous acid from nitrosylsulfuric acid with the aid of a compound that does not neutralize the advantages of the strong acid medium. This is possible by *weak* acids. Among these phosphoric acid offers the most advantages as it does not congeal even at temperatures of −20°, so that the decomposition of the diazonium compounds can be avoided; moreover it does not give rise to the formation of troublesome by-products in the reaction of coupling as *e. g.* indophenols, as is the case if glacial acetic acid is used.[4]

Experimental

2,4-Dinitraniline (3 g.) is dissolved in 15 cc. of sulfuric acid (1.84). To this solution cooled to 0° is added nitrosylsulfuric acid prepared from a little more than the theoretical quantity of sodium nitrite and 15 cc. of sulfuric acid (1.84). While stirring vigorously 60 cc. of phosphoric acid (1.7) is added, temp. 0°. After one-half hour 2 g. of urea is added and finally the reaction mixture is poured onto ice. The very weak yellow-colored diazonium solution was totally clear; no unchanged amine could be seen.

In a second experiment, in which the diazotization took place under the same circumstances, after coupling with β-naphthol in the mixture of the acids during one hour, the azo compound was isolated by pouring into water. The precipitate was boiled with ethyl alcohol. It was formed in the calculated quantity.

It appears from both experiments that the diazotization of 2,4-dinitraniline according to this new method proceeds *quantitatively.*

2,6-Dibromo-*p*-nitraniline is diazotized in the same way. The diazonium solution is poured with vigorous stirring into a concentrated solution of potassium iodide, to which some pieces of ice are added. After some hours the iodine compound is washed with water, sodium thiosulfate and finally with water again. The crude product melted at 149–150°; yield 98–99%. After some recrystallizations from alcohol, the 2,6-dibromo-4-nitroiodobenzene is separated in colorless prisms, m. p. 153.5°.

Anal. Calcd. for $C_6H_2O_2NBr_2I$: Br, 39.3; I, 31.2. Found: Br, 39.5; I, 30.9.

2,6-Dibromo-*p*-nitraniline (5.92 g.) is diazotized and coupled with 3 g. of β-naphthol in 15 cc. of glacial acetic acid. At once a rapid coupling takes place. After about one and one-half hours the mixture is poured into water. The crude product is boiled with alcohol; yield 99%, m. p. 218°; after three crystallizations from toluene, m. p. 221–222°; reddish-brown needles or prisms with a pronounced green metallic surface reflex. In sulfuric acid (1.84) the substance dissolves with red color. The alcoholic solution gives with a drop of sodium hydroxide a reddish-violet coloration.

Anal. Calcd. for $C_{16}H_9O_3N_3Br_2$: Br, 35.5. Found: Br, 35.3.

2,6-Dichloro-*p*-nitraniline (4.14 g.) is diazotized in the same way and poured into an ice-cold solution of potassium iodide; yield 6.09 g. The product was of a pale yellow

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(4) Schoutissen, *Rec. trav. chim.*, **40**, 753 (1921). After a part of the experiments based upon the above-mentioned considerations had been carried out the communication of Misslin, *Helv. Chim. Acta*, **3**, 626 (1920), appeared. His method bears much resemblance to our procedure as he releases the nitrous acid by means of glacial acetic acid.

color, m. p. 153°. The product is readily soluble in benzene and toluene, moderately in alcohol and ether. After steam distillation and crystallization from alcohol the compound was obtained as colorless needles, m. p. 153°.

Anal. Calcd. for $C_6H_2NO_2Cl_2I$: C, 22.6; H, 0.63; Cl, 22.2; I, 39.94. Found: C, 22.6; H, 0.66; Cl, 22.2; I, 39.7.

The diazo compound of this amine is coupled with β-naphthol, operating in the same way as indicated for the dibromo compound; yield 97%. The product crystallizes from boiling toluene in long, red, flattened prisms with a marked surface reflex, m. p. above 270°.

Anal. Calcd. for $C_{16}H_9O_3N_3Cl_2$: Cl, 19.5. Found: Cl, 19.4.

Picramide (3.3 g.) is dissolved in 15 cc. of nitrobenzene. To this solution is added 1 g. of sodium nitrite in 10 cc. of concentrated sulfuric acid. The mixture is cooled with salt and ice to about −10°. Now under vigorous stirring 20 cc. of phosphoric acid (1.7) is dropped into this solution, the temperature not being allowed to exceed 0°. After one-half hour 2 g. of powdered urea is added, afterward a little more than the theoretical quantity of β-naphthol. The pale yellow colored diazonium solution turns to reddish-brown. After about one-half hour the reaction mixture is poured onto water: the azo compound remains dissolved in the nitrobenzene layer. By the addition of alcohol to the nitrobenzene solution the product is isolated; yield 80–90%. The compound is crystallized from much glacial acetic acid or from boiling nitrobenzene: red needles with metallic reflex, m. p. above 260° with decomposition. The solution in sulfuric acid (1.84) is indigo blue. In alcohol, benzene and ligroin the substance is insoluble. The alcoholic suspension gives on addition of a trace of caustic potash an intense red color; in thin layers this color appears as blue however.

The diazonium solution of 5 g. of picramide is coupled with phenol. The azo compound can be isolated from the nitrobenzene layer by the addition of ligroin and carbon tetrachloride; yield nearly the theoretical. The compound dissolves in nitrobenzene, benzene, glacial acetic acid and alcohol; it is less soluble in carbon disulfide and carbon tetrachloride, very little in ligroin. The solution in sulfuric acid (1.84) is orange-yellow. The alcoholic solution gives with a drop of caustic potash a red color; in thin layers the color is blue. The azo compound dissolves in 2 *N* potassium hydroxide with a red color; this disappears however very quickly, especially when the solution is warmed.[5] The compound is crystallized from benzene and separated in short, thick needles, which show a metallic reflex, m. p. 194°.

Anal. Calcd. for $C_{12}H_7O_7N_5$: N, 21.03. Found: N, 20.74.

In the same way the product of coupling with anisole was obtained, yield about 80%. The compound was crystallized by dissolving the impure product in benzene and adding ligroin gradually as pointed, orange needles, m. p. 148°. The compound dissolves in nitrobenzene, benzene, alcohol, ether, glacial acetic acid, chloroform and acetone and is insoluble in ligroin. With sulfuric acid (1.84) an orange-yellow color appears. The color turns from yellow to red by the addition of a drop of potassium hydroxide to the alcoholic solution; this solution is also *red* in thin layers.

Anal. Calcd. for $C_{13}H_9O_7N_5$: N, 20.18. Found: N, 19.94.

The diazo solution of 5 g. of picramide was coupled with 3 g. of phenetole, yield 6.5 g. After dissolving the crude product in benzene and cautiously adding ligroin the product separated in red leaflets with metallic surface luster, m. p. 171–172°. With concentrated sulfuric acid an orange-red color appears. The alcoholic solution turns to red on the addition of alkali; in thin layers the color is red as well. It seems, therefore, that for the change in color to blue of these azo compounds, which possess several nitro groups, a free hydroxyl group is required.

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[5] According to Borsche, *Ber.*, 54, 1287 (1921), decomposition takes place, evolving nitrogen, picric acid and phenol.

Anal. Calcd. for $C_{14}H_{11}O_7N_5$: N, 19.38. Found: N, 19.11.

In the same way the product of the coupling of **2,4,6-trinitro-5-aminoanisole** with **phenol** has been isolated. After recrystallization from benzene orange needles are obtained, m. p. 165°. The yellow-orange alcoholic solution turns to red upon the addition of a drop of 2 *N* potassium hydroxide; in thin layers the color is *indigo blue*.

Anal. Calcd. for $C_{13}H_9O_8N_5$: N, 19.29. Found: N, 19.04.

The azo compound of **trinitroaminoanisole** with **anisole** crystallizes in the same way in thick, red needles; yield 82%, m. p. 118°. In concentrated sulfuric acid the substance dissolves with a yellow color. The alcoholic solution turns to red on the addition of a drop of potassium hydroxide. In thin layers the color is red as well.

Anal. Calcd. for $C_{14}H_{11}O_8N_5$: N, 18.56. Found: N, 18.34, 18.42.

2,4,6-Trinitro-5-aminophenetole can also be diazotized in exactly the same way. After coupling with *phenol* the azo compound is obtained in a yield of 82%. This substance possesses the same properties as the coupling product of trinitroaminoanisole with phenol. It crystallizes from the benzene solution upon the gradual addition of light petroleum in long orange-red needles, m. p. 149°.

The author wishes to thank the "Hoogewerff-Foundation" for the financial support in this investigation; also he is much indebted to Professor J. Böeseken, Delft, for his kind help and interest.

Summary

A new procedure of diazotization has been worked out, which, as is illustrated with several instances, creates the possibility of diazotizing very weakly basic amines.

The principle of this method is based on the one hand upon the use of concentrated sulfuric acid in order to obtain a formation of amine salt, as far as possible; on the other hand, upon the release of nitrous acid from nitrosylsulfuric acid by adding phosphoric acid.

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The Character of the Diazonium Group.[1] The Tetrazotization of Para-Phenylenediamines

BY H. A. J. SCHOUTISSEN

The use of a diazo and tetrazo compound derived from *p*-phenylenediamine has become of very great practical importance in the manufacture of azo dyes, but as it is essential that *a single compound and not a mixture of diazo and tetrazo compounds should be prepared and further, that no large excess of nitrous acid should be present these compounds have hitherto been prepared in an indirect way.* For this purpose either *p*-nitraniline or *p*-aminoacetanilide is used as the starting point. Hitherto it has not been possible to tetrazotize *p*-phenylenediamine in a quantitative way. The tetrazotization of negatively substituted *p*-phenylenediamines presents still greater difficulties.

Griess[2] found that it was impossible to convert *p*-diaminobenzoic acid into the tetrazo compound as it became exclusively *p*-aminodiazobenzoic acid. It has also been observed that nitrous acid converts only one of the amino groups of *p*-phenylenediaminosulfonic acid.[3] The same behavior is shown by 1,4-naphthalenediamino-3-sulfonic acid;[4] a similar example is *o*-nitro-*p*-phenylenediamine as appears from the researches of Bülow and Mann.[5] Benda[6] examined the possibility of tetrazotizing *p*-phenylenediaminoarsenic acid; in spite of all the methods which he applied, he only succeeded in diazotizing *one* of the two amino groups.

The question arises why these *p*-phenylenediamines are diazotized partially. Cain and Morgan[7] have tried in vain to give a satisfactory explanation. However, the present author succeeded in giving a logical explanation by observing the following rules. (1) The reaction of diazotization proceeds between the *salt* of the amine and free nitrous acid.[8] (2) The group diazonium is extremely negative, being much stronger than the nitro group.

Observing these results the author has succeeded too in finding a method of tetrazotization which gives good results for these diamines.

It is a well-known fact, that the character of aromatic amino compounds is changed in a high degree by the introduction of substituents in the nucleus. The nitro group, *e. g.*, decreases to a large extent the basicity of the aromatic amines. So, for example, 1,2-diamino-4-nitrobenzene is a monoacidic base,[9] 1,2-diamino-3,5-dinitrobenzene gives salts which are hydrolyzed into acid and free base,[10] while the salt of hydrogen chloride from 1,3-diamino-2,4,6-tribromobenzene yields hydrogen chloride when exposed to the air.[11] *p*-Phenylenediamine gives salts with both amino groups. This is still the case with monochloro-*p*-phenylenediamine[12] as well as probably with the symmetrical dichloro-*p*-phenylenediamine.[13] Bülow,[14] on the contrary, found that the salt of mononitro-*p*-phenylenediamine contains merely *one* mole of hydrogen chloride. It was found by Wolff[15] that 2,6-dichloro-*p*-phenylenediamine combines only with *one* mole of hydrogen chloride, trichloro- and dinitro-*p*-phenylenediamine have a still more reduced basicity. Krause[16] found that tetrachloro-*p*-phenylenediamine showed a basicity reduced to such an extent that he could recrystallize this compound from concentrated hydrochloric acid. In this diamine therefore the basicity of *both* the amino groups is very small. Wolff[17] found that the salts of trichloronitro-*p*-phenylenediamine are only stable in concentrated hydrochloric acid and sulfuric acid; both are hydrolyzed on diluting with water, the free base separating.

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(1) Schoutissen, *Rec. trav. chim.*, **40**, 763 (1921).

(2) Griess, *Ber.*, **17**, 603 (1884).

(3) German Patent 160,170; *Friedländer*, **8**, 133.

(4) German Patent 102,160; *Friedländer*, **5**, 508.

(5) *Ber.*, **30**, 877 (1897).

(6) Benda, *Ber.*, **44**, 3300 (1911).

(7) Cain, *J. Chem. Soc.*, **91**, 1049 (1907); Cain, "The Chemistry and Technology of the Diazo Compounds," London, 1920, p. 188–189; Morgan, *J. Chem. Soc.*, **91**, 1315, 1505 (1907); **95**, 1319 (1909); **93**, 617 (1908); **97**, 2561 (1910).

(8) Schoutissen. These, Delft, 1926.

It follows from these facts that negative substituents reduce the basicity of the amino groups in a very pronounced way. This influence of negative groups on the basicity will be strong for amino groups, in respect to which they occupy the ortho or para position; it will be less pronounced for the amino group in meta position.

Let us now consider *p*-phenylenediamine; the diazotization of *one* of the ammonium groups will present no difficulties and proceed with small concentrations of mineral acid in consequence of the relatively strong basic properties of *p*-phenylenediamine. However, as soon as the diazonium group has entered into the benzene nucleus this substituent will by its strong negative character (resembling at least 2 nitro groups at the positions ortho and para with respect to the substituent) reduce to a great extent the basicity of the second amino group in para position. Therefore it is to be expected that this amino group can only be converted into the ammonium group *and therefore into the diazonium group* with very high concentrations of mineral acid. No wonder that the tetrazotization of *p*-phenylenediamine presents great difficulties in opposition to *m*-phenylenediamine. It is to be expected that the same phenomena will be still more pronounced for the negatively substituted *p*-phenylenediamines.

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(9) Gottlieb, *Ann.*, **85**, 27 (1853).
(10) Norton and Elliott, *Ber.*, **11**, 328 (1878).
(11) This Journal, **18**, 470 (1896).
(12) Cohn, *Mitt. Techn. Gew. Mus. Wien*, **11**, 211 (1901).
(13) Möhlau, *Ber.*, **19**, 2010 (1886).
(14) Bülow, *ibid.*, **29**, 2284 (1896).
(15) Wolff, These, Berlin, 1909.
(16) Krause, *Ber.*, **12**, 51 (1879).
(17) Wolff, These, Berlin, p. 9.

Therefore the tetrazotization of *p*-phenylenediamines can be reduced to the diazotization of highly negatively substituted amines. It is to be expected that the tetrazotization of these *p*-phenylenediamines will succeed according to the method which was elaborated for the extremely weak basical amines.[18]

According to the data of literature it has not yet been posssible to tetrazotize *o*-phenylenediamine. It has been shown that by the action of nitrous acid this diamine, by internal condensation, is always converted into the *azimino compound.*[19]

This can be also explained with the same rules 1 and 2 mentioned above. The first action of nitrous acid may be the formation of *one* diazonium group. As we know, however, that the basicity of the amino group in *o*-nitroaniline has nearly disappeared, this will be still more pronounced for the remaining amino group in ortho position in this monodiazotized diamine. Tetrazotization will be possible only in very strong mineral acidic medium, otherwise the amino group is able to couple with the diazo group to an azimino compound.

Experimental

1.—***p*-Phenylenediamine chloride** (3.62 g.) is dissolved in 70 cc. of phosphoric acid (d. 1.7). This solution is then cooled in a beaker with an ice-salt mixture. With vigorous stirring a solution of 3 g. of sodium nitrite in 30 cc. of sulfuric acid (d. 1.84) is dropped into it (temp. −5°). After the addition of the nitrosylsulfuric acid the tetrazotization is still continued for about one-half hour, after which 2 g. of finely powdered urea is added. Also in the following experiments the excess of nitrous acid is removed for the purpose of giving convincing evidence that the tetrazotization proceeds really in the original solution.

The reaction mixture is poured after one-half hour into a concentrated solution of 8 g. of potassium iodide, to which some pieces of ice are added. After being kept overnight the mixture is diluted with water and the precipitate filtered off. The pale yellow precipitate is washed with water, sodium thiosulfate and water again; yield 6.5 g., calcd. 6.6 g. After treatment with norit and recrystallization from dilute ethyl alcohol, 6.1 g. of *p*-diiodobenzene was obtained, m. p. 129°. It appears from the above that in these circumstances *p*-phenylenediamine is tetrazotized quantitatively; the mother liquor after being made alkaline showed no trace of *p*-iodoaniline.

2.—The tetrazonium solution of *p*-phenylenediamine is dropped with vigorous stirring into a solution of cuprous chloride (prepared by refluxing 10.8 g. of $CuSO_4 \cdot 5H_2O$, 5.4 g. of NaCl, 45 cc. of water, 150 cc. of HCl (1.19) and 30 g. of copper) cooled to 0°. *p*-Dichlorobenzene passed over on steam distillation; yield about 70% of colorless *p*-dichlorobenzene, m. p. 53°.

3.—A solution of 15 g. of bromine in 15 g. of potassium bromide and 100 cc. of water is cooled with ice. On dropping the tetrazonium solution with vigorous stirring into the latter a red precipitate of the perbromide separates. After one hour copper powder is added with vigorous stirring. On standing overnight the precipitate is filtered off, extracted twice with small quantities of alcohol and filtered again. On diluting the solution with water a white precipitate separates, which is recrystallized from boiling dilute alcohol as beautiful long colorless needles of *p*-dibromobenzene, m. p. 87.5°.

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(18) Schoutissen, These, Delft, 1926; THIS JOURNAL, **55**, 4531 (1933).

(19) Ladenburg, *Ber.*, **9**, 219 (1876)· **17**, 147 (1884).

4.—The perbromide of the tetrazonium compound of *p*-phenylenediamine is suspended in ice water and gradually added with vigorous stirring to 100 cc. of concentrated ammonia, temp. 0°. The crude product is filtered off and purified by steam distillation; yield 2.2 g. On recrystallization from warm alcohol the substance appears in beautiful hexagonal leaflets, m. p. 83°. The properties correspond with those of bis-triazobenzene, described by Griess.[20]

p-Phenylenediamine sulfonic acid is tetrazotized in the same way. The tetrazonium solution is dropped into potassium iodide cooled with ice and salt. Instantly a strong evolution of nitrogen begins. After being kept for two and one-half hours at 0° the solution is gradually warmed and free iodine is removed by steam distillation. The diiodide separates on cooling in flat pointed needles. It is easily soluble in water, slightly soluble in strong mineral acids, moderately soluble in ether.[21]

The barium salt was prepared by adding a concentrated solution of barium chloride to the warm solution of the ammonium salt. It was obtained in long, bright leaflets; at 160° these crystals lose their water of crystallization.

The potassium salt was obtained in a similar way; it crystallizes in long, colorless needles with 1 mole of water of crystallization. After removing this water the potassium salt of 1,4-diiodobenzene sulfonic acid was treated with phosphorus pentachloride by heating to 100–140°; m. p. of the crude product after extraction with water 130°. After one crystallization from cold chloroform the sulfochloride is obtained in colorless needles, m. p. 131.[21] The compound dissolves readily in ether and chloroform and is insoluble in water.

If a quick stream of chlorine dried by sulfuric acid is passed through the solution of this compound in chloroform, the 1,4-diiodobenzene sulfochloride-dichloride precipitates. It crystallizes in pale yellow, short, sparkling quadrilateral prisms, m. p. 128°.[21]

Nitro-p-phenylenediamine is tetrazotized according to the indications given above. The tetrazonium solution is poured after about one and one-half hours into a concentrated solution of potassium iodide. A dark resin was formed. After the mixture has been kept overnight it is isolated and washed with water. After adding 50 cc. of 2 *N* potassium hydroxide diiodonitrobenzene passed over on steam distillation; yield 1 g. of crude product, m. p. 109°. The compound crystallizes from petroleum ether in weak yellow needles, m. p. 109–110°. It appears from the melting point and the analysis that this product is really 2,5-diiodonitrobenzene.

Anal. Calcd. for $C_6H_3NO_2I_2$: I, 67.72. Found: I, 67.63, 67.59.

The non-volatile mass is acidified with dilute sulfuric acid. On steaming a yellow product (1 g.) passed over. This compound was freed from iodine by a sodium thiosulfate solution and afterward purified from small quantities of mixed diiodonitrobenzene by dissolving it in 2 *N* alkali, m. p. of the crude product 80–81°. The compound crystallized from boiling petroleum ether in big citron yellow, quadrilateral prisms, m. p. 81°. In sodium hydroxide the substance dissolves with an orange-red color; the salt crystallizes in red needles.

Anal. Calcd. for $C_6H_4O_3NI$: I, 47.91. Found: I, 47.9, 48.0.

It appears from analysis and m. p. that the compound is 4-iodo-2-nitrophenol. The origin of this by-product can be explained from the easy decomposition of the tetrazonium compound while it is being poured into the potassium iodide solution. No unaltered amine could be shown in the filtrate.

2,5-Dichloro-p-phenylenediamine was dissolved in concentrated sulfuric acid, mixed with the theoretical quantity of nitrosylsulfuric acid and dropped into twice the volume of phosphoric acid (d. 1.7) temp. −10–0°. The tetrazonium solution thus obtained was dropped into cuprous chloride (obtained by boiling 10.8 g. of $CuSO_4 \cdot 5H_2O$, 5.4 g. of NaCl, 45 g. of water, 90 cc. of HCl (1.19) and 31 g. of copper powder), to which some pieces of ice are added. After some time the reaction mixture is warmed to 60° and afterward diluted with water; the precipitate is filtered off and extracted by hot benzene. Upon evaporating the benzene solution tetrachlorobenzene crystallizes; yield 64%, m. p. 131°. After one recrystallization from alcohol colorless needles were obtained identical with 1,2,4,5-tetrachlorobenzene.[22]

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[20] Griess, *Ber.*, **21**, 1559 (1888).

[21] Boyle, *J. Chem. Soc.*, 1701 (1909).

2,6-Dichloro-*p*-phenylenediamine is tetrazotized in the same way as the 2,5 compound. The weak red colored tetrazonium solution is then poured into a solution of 20 g. of cuprous chloride in 100 cc. of hydrochloric acid (1.19) and 150 cc. of water, temp. about 20°. Instantly a strong evolution of nitrogen begins and after the reaction mixture has been warmed for two hours to 80° the precipitate is filtered off. By steaming the alkaline suspension 1,2,4,6-tetrachlorobenzene is obtained; on recrystallization from ethyl alcohol colorless needles, m. p. 50–51°.[23]

Anal. Calcd. for $C_6H_2Cl_4$: C, 33.4; H, 0.9; Cl, 65.7. Found: C, 33.5; H, 0.8; Cl, 65.3.

2,6-Dibromo-*p*-phenylenediamine is tetrazotized in exactly the same way. The reaction mixture is dropped into a concentrated aqueous solution of potassium iodide to which some pieces of ice are added. After the mass has been kept overnight the precipitate is filtered off and washed with sodium thiosulfate and water; yield 95%. The compound was purified by recrystallization from warm alcohol 1:1 after decoloration with norit as colorless needles, m. p. 115°. It is easily soluble in benzene and chloroform, likewise in alcohol, ether and carbon tetrachloride, little however in petroleum ether.

Anal. Calcd. for $C_6H_2Br_2I_2$: Br, 32.78; I, 52.05. Found: Br, 32.4; I, 51.8.

The filtrate, obtained after converting the tetrazonium solution with potassium iodide, was made alkaline; no precipitate of 2,6-dibromo-4-iodoaniline has been observed. The diamine has been tetrazotized quantitatively.

Trichloro-*p*-phenylenediamine.—Twenty grams of 2,6-dichloro-*p*-phenylenediamine is dissolved in 100 cc. of acetic anhydride; in order to catalyze the acetylation a drop of concentrated sulfuric acid is added. The reaction mixture is boiled for some time under a reflux condenser. After the addition of 50 cc. of glacial acetic acid the solution is poured into water; the diacetyl product separates in small colorless needles. It is recrystallized from glacial acetic acid, m. p. 225°. At room temperature the diacetyl compound is little soluble in the usual solvents; on warming it dissolves readily in ethyl alcohol (96%) and glacial acetic acid. The chlorination of this compound cannot be carried out in a direct way with free chlorine; however, the interaction of calcium hypochlorite is successful.[15]

A solution of $^3/_{20}$ mole of $Ca(OCl)_2$ is added in small quantities to a solution of 13 g. ($^1/_{20}$ mole) of diacetyldichloro-*p*-phenylenediamine in 150 cc. of glacial acetic acid. In the beginning a yellow tough mass is obtained which however in a few days turns into the crystalline state. Moreover colorless crystals separate from the mother liquor. The crude product is crystallized from glacial acetic acid and finally from 96% alcohol as small colorless needles, m. p. 289°.

The diacetyltrichloro-*p*-phenylenediamine has been saponified with 70% sulfuric acid. The diamine is precipitated from this solution by adding ammonia. It can be crystallized by the gradual addition of ligroin to the solution in chloroform. In this way the diamine is obtained in colorless needles, m. p. 198°. The compound dissolves readily in the usual solvents, little however in water.

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[22] *Ann.*, **152**, 248 (1869); **192**, 236 (1878); **296**, 67 (1897); *Ber.*, **29**, 875 (1896).

[23] *Ann.*, **141**, 105 (1867); **192**, 237 (1878).

It is tetrazotized in exactly the same way as described for 2,5-dichloro-*p*-phenylenediamine. The tetrazonium solution is dropped with vigorous stirring into a solution of cuprous chloride in hydrochloric acid cooled to 0°. After one hour the solution is warmed to 60° and then the pentachlorobenzene is steamed over. The compound separates in colorless crystals, yield 80%. It is recrystallized with warm alcohol (60%); on cooling it separates in long colorless needles, m. p. 86–87°.[24]

***o*-Phenylenediamine**, 3.24 g., finely powdered, m. p. 102°, is tetrazotized in the same way, the temperature not being allowed to exceed −5°. About one hour after the first addition of phosphoric acid (1.7) the tetrazotization has ceased and the reaction mixture is poured into a solution of 25 g. of potassium iodide in 100 cc. of water to which some pieces of ice are added A brown oil separates with a strong evolution of nitrogen. After the mixture has been kept for twelve hours at room temperature, the reaction is brought to an end by warming. The iodine is removed with sodium bisulfite. The *o*-diiodobenzene has been separated by steam distillation. The formed weak yellow oil has been shaken with dilute potassium hydroxide to remove the eventually formed *o*-iodophenol. The oil is washed with water and finally dried in a desiccator over concentrated sulfuric acid; yield about 1 g. The boiling point,[25] as the average of several determinations, was found to be 287°, 768.5 mm. This agrees with the b. p. of *o*-diiodobenzene.[26] After steaming, 2.5 g. of resinous product remains which solidifies after cooling to a brownish mass. We have not succeeded in separating definite compounds from this product.

The author wishes to thank the "Hoogewerff-Foundation" for the financial support in this investigation; also he is much indebted to Professor J. Böeseken, Delft, for his kind help and interest in the above-mentioned experiments.

Summary

1. The technical importance of a method of tetrazotizing *p*-phenylenediamine and its substituted derivatives in a quantitative way has been shown.

2. Starting from the very negative character of the diazonium group and taking account of the fact that the reaction of diazotization proceeds between the *salt* of the amine and nitrous acid a logical and simple explanation is given why negatively substituted *p*-phenylenediamines could only be diazotized hitherto at *one* of the amino groups. Therefore the theories of Cain and of Morgan on this subject must be cast aside.

3. The tetrazotization of *p*-phenylenediamines corresponds with the diazotization of very negatively substituted amines. The same procedure which makes possible diazotizing these amines also serves in tetrazotization of *p*-phenylenediamines. *p*-Phenylenediamine and its derivatives, *e. g.*, nitro-*p*-phenylenediamine, *p*-phenylenediamine sulfonic acid, 2,5-dichloro-*p*-phenylenediamine, 2,6-dichloro-*p*-phenylenediamine, 2,6-dibromo-*p*-phenylenediamine, trichloro-*p*-phenylenediamine, can be tetrazotized in a quantitative way. The two diazo groups were eliminated with cuprous chloride or potassium iodide with a good yield.

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(24) *Ann.*, **141**, 96, 152, 247 (1867); **154**, 182 (1870); **172**, 344 (1874).

(25) Determined after the method of Siwoloboff, *Ber.*, **19**, 795 (1886); Tschitschibabin and Jelgasin, *ibid.*, **47**, 1848 (1914).

(26) Körner and Wender found 286.5°, 751 mm., *Gazz. chim. ital.*, **17**, 491 (1887).

4. It appears that *o*-phenylenediamine is tetrazotizable; however, as would be expected, different factors (lesser stability of the tetrazo compound, coupling with products of decomposition and the formation of an azimino compound) have an unfavorable influence on the yield.

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[CONTRIBUTION FROM THE LABORATORY FOR ORGANIC CHEMISTRY OF THE TECHNICAL HIGH SCHOOL, DELFT, HOLLAND]

The Character of the Diazonium Group.[1] A New Method of Preparing Mixed Disazo Dyestuffs[2]

BY H. A. J. SCHOUTISSEN

It is a well-known fact that the equilibrium diazonium $\rightleftarrows$ diazo shifts with the alteration of the concentration of mineral acid: acids transpose the diazo into the diazonium compound. Substituents in the nucleus also have a pronounced influence upon the situation of this equilibrium.[3] The equilibrium shifts to diazo compound if the substituents are more negative. As the reaction of coupling takes place between the *diazo* compound and the azo component in connection with the experiments of Hantzsch on the situation of the equilibrium diazonium $\rightleftarrows$ diazo for different diazo compounds, it may be expected that diazo compounds with strong negative substituents in the nucleus will be able to couple in much greater concentrations of mineral acid as compared with the less negatively or positively substituted diazo compounds. For, notwithstanding the great concentration of mineral acid, still a proper amount of diazo compound is present for the former. K. H. Meyer and Lehnard[4] found that not only phenols and naphthols but also their ethers are capable of coupling with some diazo compounds. The reaction of coupling however proceeds much more slowly with the ethers in comparison with the respective phenols and naphthols and proceeds only rapidly in a mineral acid solution if the diazo compound is *very negatively* substituted. Table I shows the comparative behavior of some diazo compounds with regard to β-naphthol and anisole as to the velocity of the reaction of coupling in a medium of 1 volume of sulfuric acid (d. 1.84) and 2 volumes of phosphoric acid (d. 1.7).

It appears that coupling with anisole proceeds only if *two nitro groups* in the positions ortho and para with respect to the diazo group are present. If two nitro groups are in meta position and their negative influence upon the diazo group therefore is smaller, no coupling appears with ethers. A similar behavior follows from the experiments with β-naphthol.

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(1) Schoutissen, *Rec. trav. chim.*, **40**, 763 (1921).

(2) Schoutissen, communicated in the section meeting for applied chemistry of the Dutch Chem. Soc., April 21, 1922, Delft; see also *Chemisch Weekblad*, **19**, 217 (1922).

(3) Hantzsch, *Ber.*, **33**, 2166 (1900).

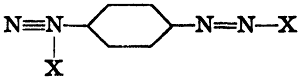
(4) K. H. Meyer and Lehnard, *Ann.*, **398**, 74 (1913).

Table I makes it possible to limit the character of a negative substituent in a relatively simple way. Now in the tetrazotized *p*-phenylenediamine *one* diazonium group behaves according to the nature of the *second.* Therefore, if the diazonium group is an extraordinarily strong negative group, it may be expected that the tetrazotized *p*-phenylenediamine couples as well as diazotized 2,4-dinitroaniline with β-naphthol and anisole in the same conditions; if, however, this group is less negative, at most coupling with β-naphthol appears.

Table I

Diazotized	Azo component β-Naphthol	Anisole
Aniline	No coloration	No coloration
p-Toluidine	No coloration	No coloration
p-Anisidine	No coloration	No coloration
p-Aminophenol	No coloration	No coloration
p-Chloroaniline	No coloration	No coloration
p-Bromoaniline	No coloration	No coloration
p-Iodoaniline	No coloration	No coloration
p-Aminobenzoic acid	No coloration	No coloration
Sulfanilic acid	No coloration	No coloration
2,4-Dichloroaniline	No coloration	No coloration
2,4-Dibromoaniline	No coloration	No coloration
2,4,6-Trichloroaniline	Couples slowly	No coloration
2,4,6-Tribromoaniline	Couples slowly	No coloration
p-Nitraniline	Couples quickly	Couples very slowly
2-Chloro-*p*-nitraniline	Couples quickly	Couples very slowly
2-Bromo-*p*-nitraniline	Couples quickly	Couples very slowly
2,6-Dichloro-*p*-nitraniline	Couples quickly	Couples slowly
2,6-Dibromo-*p*-nitraniline	Couples quickly	Couples slowly
3,5-Dinitroaniline	Couples quickly	No coloration
2,4-Dinitraniline	Couples very quickly	Couples quickly
2,4,6-Trinitroanisidine	Couples very quickly	Couples quickly
2,4,6-Trinitrophenetidine	Couples very quickly	Couples quickly
2,4,6-Trinitroaniline	Couples very quickly	Couples very quickly
p-Phenylenediamine (tetrazotized)	Couples very quickly	Couples quickly
Benzidine (tetrazotized)	No coloration	No coloration

For, as a strong negative substituent, the one diazonium group effects the transmutation of the other diazonium group to diazo



and gives in this way the possibility of coupling this *diazo* group in the strong acidic medium with β-naphthol; moreover, it may be expected that in consequence of the increased energy of coupling this diazo-diazonium compound couples with ethers such as anisole.

If the speculations mentioned above are exact, it may be predicted also that the coupling *will be restricted to this diazo group,* for as soon as the present diazo group has coupled with a component an *azo* group has been formed, whose nature at most is weakly negative. The remaining diazonium group therefore is not able to change into *diazo* condition in this strongly acidic medium, and it will be possible only to couple this group with an azo component in a weakly basic or weakly acidic solution. The experiments have confirmed our expectations absolutely. The technical importance of this method of procedure, based entirely upon theoretical arguments, appears if one considers the modern preparation of disazo dyes derived from *p*-phenylenediamine.[5]

Operating under the conditions outined below one attains the object more quickly. In the strongly acidic solution a quantitative tetrazotization is accomplished[6] and after that a coupling of one of the diazo groups. Afterward the second desired azo component is introduced under normal circumstances of coupling.

This method enables one at the same time to couple with azo components (e. g., ethers) in the first phase, which is not possible with one of the other methods and which gives an insensibility of the dyes to alkalies. Incidentally it may be observed that the behavior of tetrazotized benzidine in strongly acidic medium in regard to β-naphthol and anisole points to the fact that two substituents in different nuclei influence each other only to a small degree.

Experimental

1.—With warming 2.16 g. of *p*-phenylenediamine is dissolved in 70 cc. of phosphoric acid (1.7). This solution is cooled with stirring with ice and salt. Afterward nitrosylsulfuric acid prepared from 2.88 g. of sodium nitrite and 30 cc. of sulfuric acid (1.84) is added by drops, temp. about −5°. After one-half hour, in order to eliminate the excess of nitrous acid, 2 g. of finely powdered urea is added. After one-half hour a large excess of β-naphthol dissolved in a small quantity of glacial acetic acid is added. After three-fourths hour the mixture is poured into ice water. The *diazonium-diazo compound* separates from this dilute solution (especially after the addition of sodium chloride), in orange-yellow needles, and may be recrystallized from water at 40° without decomposition. As the product obtained dissolves in water it may be concluded that *no disazo compound is formed.* Dilute alkali solution gives a blue coloration (reaction of Nietzki–Meldola for the diazo-azo compounds.

The crude product is now poured into a solution of potassium carbonate cooled at 0° and coupled a second time with β-naphthol. After two hours the disazo compound is filtered off and washed with 2 *N* potassium hydroxide, yield 96%. It is soluble in boiling alcohol and dilute alkalies. The alcoholic suspension gives a violet coloration with a drop of 2 *N* alkali. The compound crystallizes from boiling aniline in small needles with a greenish surface reflex. It dissolves with a beautiful blue color in concentrated sulfuric acid. If this solution is warmed for some time to 100° the compound is sulfonized; on diluting with water no precipitate appears. The product obtained in this way dissolves in dilute alkalies with a beautiful blue color.

Anal. Calcd. for $C_{26}H_{18}N_4O_2$: C, 74.61; H, 5.31. Found: C, 74.48; H, 5.37.

2.—2.16 g. of *p*-phenylenediamine is tetrazotized according to the procedure given under 1. After coupling with 2.88 g. of β-naphthol the diazo-azo compound is combined with phenol; yield 99%. The alcoholic solution becomes blue-violet upon the addition

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(5) Compare Cain, "The Chemistry and Techn. of the Diazo Compounds," p. 25.

(6) Schoutissen, THIS JOURNAL, **55**, 4535 (1933).

of a little ammonia. The compound crystallizes from methyl alcohol in long filaments or as needles combined to rosets with a greenish surface reflex, m. p. 231–232°. In dilute alkalies the compound dissolves red-violet, in concentrated sulfuric acid greenish-blue.[7]

3.—This time the reaction of coupling is performed with phenol and β-naphthol just as under 2, but in the reversed order of succession; yield 98.5%. The compound appeared to be identical with the disazo compound described under 2, m. p. 231–232°.

4.—2.16 g. of *p*-phenylenediamine is tetrazotized according to the method given under 1. Now the coupling in the strongly acidic medium is performed with 3.5 g. of β-naphthol methyl ether dissolved in 20 cc. of glacial acetic acid, and afterward in potassium solution with 2 g. of phenol; yield nearly the theoretical. The excess of β-naphthol ether is removed by boiling with ether; m. p. of the undissolved portion 229°; after one recrystallization from methyl alcohol m. p. 231°; m. p. of the mixture with β-naphthol-azobenzene-azophenol, 231°. It appears therefore that during the coupling all the naphthol ether is saponified.

5.—Now first of all the tetrazotized *p*-phenylenediamine is coupled with α-naphthol and secondly with phenol. Again the typical coloration to blue has been observed. After two hours the dye is filtered off and washed with dilute alcohol; yield 6.9 g.; theoretical, 7.36 g. In dilute alkalies the compound dissolves red, in concentrated sulfuric acid with an indigo blue color.[7]

6.—The tetrazotized *p*-phenylenediamine is coupled with phenol in two stages. The greenish-yellow precipitate is filtered off and washed with 2 *N* hydrochloric acid and water; yield nearly the theoretical. The compound can be crystallized from hot aniline. On cooling brass-colored leaflets separate which are washed with dilute hydrochloric acid. The substance is recrystallized from boiling benzene: square to lozenge-shaped leaflets, m. p. with decomposition 270°. From 1:1 alcohol it crystallizes in fine, greenish-yellow, silk gleaming crystals. In alkalies the compound dissolves with a red color, in concentrated sulfuric acid with a pure blue color. It is insoluble in petroleum ether and carbon tetrachloride.[7]

7.—The tetrazonium solution is coupled in a first step with 5 g. of anisole and afterward with phenol. During the reaction of coupling in the second stage the color changes from blue to yellow-green. After two hours the disazo compound is filtered off and washed with water; yield nearly the theoretical quantity. It is recrystallized from aniline at 100°; on cooling the disazo compound separates in orange, chaff-shaped leaflets. The crystals are washed with cold aniline, benzene and petroleum ether and finally with dilute hydrochloric acid. After recrystallization from benzene the melting point was found to be 206–207°. The disazo compound dissolves in dilute alkalies with a beautiful red color.

Anal. Calcd. for $C_{19}H_{16}N_4O_2$: N, 16.87. Found: N, 16.72.

8.—2.16 g. of *p*-phenylenediamine is tetrazotized according to the method described under 1. Now 3 g. of phenetole, dissolved in 5 cc. of glacial acetic acid is added to the tetrazonium solution; afterward the diazo-azo compound is coupled with phenol in potassium carbonate solution; yield 6.4 g., calcd. 6.92 g. The crude product is crystallized from aniline at 100° as orange, chaff-shaped leaflets. After washing with dilute hydrochloric acid and recrystallization from boiling benzene the compound is obtained in greenish-yellow leaflets, m. p. 179°.

The compound dissolves readily in warm aniline, less in alcohol, acetone, benzene and toluene and is insoluble in carbon tetrachloride and petroleum ether. With dilute alkalies a beautiful red color appears; in concentrated sulfuric acid the compound dissolves with a blue color, in thick layers the color is red.

Anal. Calcd. for $C_{20}H_{18}N_4O_2$: N, 16.18. Found: N, 15.95, 16.12.

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(7) Meldola, *J. Chem. Soc.*, **47**, 657 (1885).

Explanation of Table I.—0.02 Mole of the amines mentioned in this table is dissolved in sulfuric acid (15 cc. (d. 1.84)) and after cooling to 0° mixed with a solution of 1.44 g. of sodium nitrite in 15 cc. of sulfuric acid (1.84). Now the mixture is dropped into 60 cc. of phosphoric acid (1.7), cooled with an ice and salt mixture to −10°. After the addition of the final quantity of nitrosylsulfuric acid, the diazotization (tetrazotization) is still continued for one-half hour; afterward 2 g. of finely powdered urea is added in order to remove nitrous acid, for this might involve the production of colored matters in consequence of the nitrosation of the azo component. For each case the velocity of the reaction of coupling has been studied during one and one-half hours with the azo components β-naphthol and anisole, by determination of the quantity of dye which is produced in a definite time. *It appears from these observations that the character of the diazonium group is at least as strongly negative as the behavior of two nitro groups in the positions ortho and para with respect to the substituent.*

The author wishes to thank the "Hoogewerff Foundation" for the financial support in this investigation; he is also much obliged to Professor J. Böeseken, Delft, for his kind help and interest in this investigation.

Summary

1. The character of the diazonium group agrees with the influence of *two nitro groups* in the positions ortho and para with respect to the substituent.

2. Tetrazotized *p*-phenylenediamine couples only with *one* mole of the azo component (both *phenols and ethers*) in strongly acidic medium. These diazo-azo compounds can be isolated by pouring onto water and may be afterwards coupled with an azo compound (not with ethers).

ROTTERDAM, HOLLAND

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[CONTRIBUTION FROM THE LABORATORY FOR ORGANIC CHEMISTRY OF THE TECHNICAL HIGH SCHOOL, DELFT, HOLLAND]

The Preparation of Para-Phenylene Dihydrazine Hydrochloride

BY H. A. J. SCHOUTISSEN

In previous communications[1] a method was described by which it was possible to tetrazotize *p*-phenylenediamine in a quantitative way. Now it is of interest to investigate whether this method will enable us to prepare the *p*-dihydrazinobenzene previously looked for in vain,[2] by reduction of the corresponding tetrazonium compound with stannous chloride, according to the method of V. Meyer and Lecco.[3]

In spite of different attempts to isolate the *free* dihydrazine, I did not succeed, since this compound has a low degree of stability in aqueous

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(1) Schoutissen, These, Delft, 1926, p. 106; THIS JOURNAL, 55, 4535, 4541 (1933).

(2) Stollé and Leffler, *Ber.*, 57, 1061 (1924); compare also Wieland, Juchum and Maier, *ibid.*, 64, 2513 (1931).

(3) V. Meyer and Lecco, *Ber.*, 16, 2976 (1883).

solutions. However, the hydrochloride was prepared and analyzed. For further evidence *p*-chlorobenzene and *p*-diiodobenzene and also the disemicarbazide were prepared from the dihydrazino salt.

The researches are being continued, especially with regard to the condensation products of *p*-phenylenedihydrazine with aldehydes and ketones.

Experimental

1.—3.24 g. of *p*-phenylenediamine is dissolved with warming in 100 cc of phosphoric acid (d. 1.7). Nitrosylsulfuric acid (4.32 g. of sodium nitrite and 45 cc. of sulfuric acid (d. 1.84)) is added by drops; time 1 hour, temp. −5°. The solution obtained in this way is poured, with vigorous stirring, into a solution of 35 g. of stannous chloride dissolved in 80 cc. of concentrated hydrochloric acid, cooled at −10°. After one and one-half hours the reduction is stopped, concentrated hydrochloric acid is added and the precipitate deposits in needles. The crude product obtained by filtration is washed with concentrated hydrochloric acid. It is readily soluble in water; this solution becomes quickly colored. On warming it a little a rapid evolution of nitrogen appears. The crude product is dissolved in a small quantity of cold distilled water and filtered. Now the same volume of 2 *N* hydrochloric acid is added, besides some drops of stannous chloride solution. The hydrochloride separates in colorless flat needles. After this crystallization is repeated the precipitate is filtered off and washed successively with 1:1 hydrochloric acid, alcohol and ether. The melting point of the salt could not be determined; on warming a vigorous decomposition has been observed.

Anal. Calcd. for $C_6H_{12}N_4Cl_2$: C, 34.10; N, 26.55. Found: C, 34.09; N, 26.42.

2.—3.24 g. of *p*-phenylenediamine is tetrazotized and reduced in the same way as has been described under 1. The collected precipitate is dissolved in a small quantity of ice-cold water and introduced into a saturated solution of 25 g. of copper sulfate (crystallized). Instantly an evolution of nitrogen begins. The resulting *p*-dichlorobenzene is distilled with steam; yield 2 g., m. p. 53°.

3.—The crude product, according to 1, is dissolved in ice-cold distilled water and a little more than the theoretical quantity of iodine in potassium iodide is added. At once greenish sparkling leaflets or needles separate. If these are warmed in the solution the color turns to brown-red with evolution of gas. After the crystals have been collected and washed with sodium thiosulfate solution, the crude product consists of pale yellow-brown lozenge-shaped crystals, which become colorless on recrystallization from dilute alcohol. The melting point of 128° indicates that the substance is *p*-diiodobenzene.

4.—3 g. of *p*-phenylene dihydrazine hydrochloride, prepared after the method described under 1, is dissolved in 200 cc. of cold distilled water. Now a solution is added of 3 g. of potassium cyanate in 20 cc. of water. A colorless, crystalline precipitate separates. The crude product is recrystallized from distilled water. On cooling slowly pale yellow needles or prisms separate; yield about 2 g. The compound is slightly soluble in the usual organic solvents. No sharp melting point is observed; upon warming the substance colors and carbonizes.

Anal. Calcd. for $C_8H_{12}O_2N_6$: C, 42.85; N, 37.5. Found: C, 42.44; N, 37.72.

The author wishes to thank the "Hoogewerff-Foundation" for the support in this investigation; also he is much obliged to Professor J. Böeseken, Delft, for his kind help and interest.

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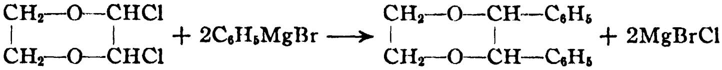
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Synthesis of Homologs of Dioxane

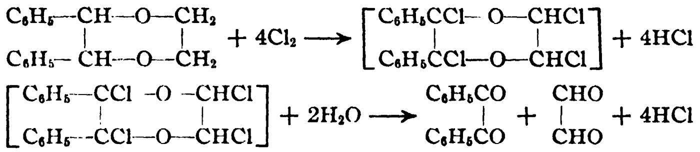
BY ROBERT CHRIST AND R. K. SUMMERBELL

A. **Diphenyldioxane.**—The excellent work on the chlorination of dioxane by Böeseken and his co-workers[1] provides a convenient starting material for a synthesis of the homologs of dioxane. 2,3-Dichlorodioxane is readily obtained in large yield by chlorination of dioxane. As the two chlorine atoms which it contains are alpha to oxygen atoms, they should be reactive to the Grignard reagent. This was found to be the case. Two moles of phenylmagnesium bromide react smoothly with one mole of 2,3-dichlorodioxane to yield 60% of the 2,3-diphenyldioxane.



$$\begin{array}{l} CH_2{-}O{-}CHCl \\ | \qquad\quad | \\ CH_2{-}O{-}CHCl \end{array} + 2C_6H_5MgBr \longrightarrow \begin{array}{l} CH_2{-}O{-}CH{-}C_6H_5 \\ | \qquad\quad | \\ CH_2{-}O{-}CH{-}C_6H_5 \end{array} + 2MgBrCl$$

The structure of the product was proved by chlorination and hydrolysis to benzil.



$$\begin{array}{l} C_6H_5{-}CH{-}O{-}CH_2 \\ \qquad\ | \qquad\ | \\ C_6H_5{-}CH{-}O{-}CH_2 \end{array} + 4Cl_2 \longrightarrow \left[\begin{array}{l} C_6H_5CCl{-}O{-}CHCl \\ \qquad | \qquad\ | \\ C_6H_5CCl{-}O{-}CHCl \end{array}\right] + 4HCl$$

$$\left[\begin{array}{l} C_6H_5{-}CCl{-}O{-}CHCl \\ \qquad\ | \qquad\ | \\ C_6H_5{-}CCl{-}O{-}CHCl \end{array}\right] + 2H_2O \longrightarrow \begin{array}{c} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + \begin{array}{c} CHO \\ | \\ CHO \end{array} + 4HCl$$

The intermediate tetrachlorodiphenyldioxane was not isolated, but its formation was indicated by the hydrolysis products, benzil and glyoxal, which were identified.

B. **Tetrachlorodioxanes.**—In a previous note[2] we confirmed the results of Butler and Cretcher on the symmetrical tetrachlorodioxane, m. p. 143–144°, and also on the unsymmetrical product, b. p. 93–95° at 11–12 mm. In addition we obtained a new symmetrical tetrachlorodioxane of m. p. 70°. This gave two molecular equivalents of glyoxal-*p*-nitrophenylosazone after hydrolysis with water and treatment with *p*-nitrophenylhydrazine.

C. **Catecholdioxane.**—The catechol derivative of dichlorodioxane which we mentioned previously[2] has since been described by Böeseken.[3] He also has obtained only one isomer whereas two would be predicted on the basis of the condensation with glycol. However, in the majority of condensations described so far, only one isomer is obtained, so that glycol is the exception rather than the rule. This might be explained by assuming that the 2,3-dichlorodioxane is not a mixture of *cis* and *trans* isomers but rather the pure *cis* isomer.

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(1) Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).

(2) Summerbell and Christ, THIS JOURNAL, **54**, 3777 (1932).

(3) Böeseken, Tellegen and Henriquez, *ibid.*, **55**, 1284 (1933).

Experimental

I. Diphenyldioxane.—(a) An ethereal solution of the phenylmagnesium bromide was prepared in the usual manner using 16 g. of magnesium, 104 g. of phenyl bromide and 300 cc. of ether; 52 g. of dichlorodioxane dissolved in 100 cc. of ether was then added slowly over a period of one and one-half hours. The reaction mixture was decomposed with water at 0° and enough sulfuric acid added to dissolve the magnesium hydroxide. The ether layer was separated and the ether distilled off. The viscous liquid remaining could not be crystallized. Upon distillation under reduced pressure the liquid solidified in the condenser. After three crystallizations from petroleum ether 48 g. of pure product was obtained, m. p. 49°, yield 60%.

Anal. Calcd.: mol. wt., 240; C, 80; H, 6.67. Found: mol. wt., 231; C, 79.75; H, 6.66.

(b) **Proof of Structure.**—6.1 g. of diphenyldioxane was chlorinated for a period of twenty-four hours at a temperature of 125°. The mixture was then hydrolyzed by boiling with water. The resulting product was extracted with petroleum ether and 1.6 g. of benzil finally crystallized out, m. p. 95°. A mixed m. p. with an authentic specimen gave 95°. A small amount of the diphenyldioxane was recovered. On treating the water solution from the hydrolysis with phenylhydrazine a very slight amount of the osazone of glyoxal was obtained, m. p. 167–168°, mixed m. p. 167°.

II. Tetrachlorodioxanes.—One hundred grams of the 2,3-dichlorodioxane was chlorinated for a period of twenty hours at a temperature of 115°. The product was distilled under reduced pressure; 52 g. of dichlorodioxane was recovered and 38 g. of the liquid unsymmetrical tetrachlorodioxane of b. p. 93–95° at 11–12 mm. described by Butler and Cretcher was obtained. Upon cooling the last fractions from the distillation a solid mass of crystals was obtained. Upon fractional crystallization using petroleum ether, 15 g. of the needle-like crystals of the symmetrical tetrachlorodioxane of Butler and Cretcher having a m. p. of 143° was obtained. Using very slow crystallization about 4 g. of a new symmetrical product of m. p. 70° was obtained. It had a crystalline form entirely different from the needles mentioned above and could easily be separated by picking out by hand. The crystals are large, flat and slightly elongated and are apparently orthorhombic and occur in aggregates.

Anal. Calcd. for $C_4H_4O_2Cl_4$: mol. wt., 226; Cl, 62.81. Found: mol. wt., 232; Cl, 62.86.

Upon decomposing 0.3550 g. with water in a sealed tube and treating with *p*-nitrophenylhydrazine, 1.01 g. of the *p*-nitrophenylosazone was obtained.

Summary

1. A new synthesis of 2,3-disubstituted dioxanes is reported.
2. 2,3-Diphenyldioxane is described for the first time.
3. A new symmetrical tetrachlorodioxane was obtained.

EVANSTON, ILLINOIS

RECEIVED MAY 15, 1933
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

A New Synthesis for Alkyl and Aryl Substituted Coumaranes

BY JOSEPH B. NIEDERL AND EDWARD A. STORCH[1]

Theoretical Part

Various methods have been applied to the synthesis of coumarane (benzo-dihydrofuran)[2] and substituted coumaranes.[3] Many of the methods reported for the preparation of alkyl and aryl substituted benzo-dihydrofurans do not appear to be completely satisfactory from the standpoint of yield, directness and generality. The process here described appears to be simpler and more direct; it furnishes comparatively good yields and seems to be more widely applicable, since it involves the condensation of an unsaturated alcohol with a phenol.

Alkylated Coumaranes.—Very briefly, the synthesis involves the condensation of allyl alcohol with phenol or cresols in the presence of a sulfuric–glacial acetic acid mixture. After heating the solution for five hours, water is added. The resulting polymer is decomposed pyrolytically. The alkyl substituted coumaranes are obtained along with small quantities of isopropenylphenol.

Allyl Alcohol–*p*-Cresol Condensation.—On depolymerization of the condensation product, a small quantity of an alkali soluble material was obtained along with the alkali-insoluble dimethylcoumarane. The former was identical with 4-methyl-2-isopropenyl phenol (III).[4] The alkali-insoluble material was shown to be 2,4-dimethylcoumarane (IV) in that it agreed in properties with this product reported in the literature.[5]

The reaction mechanism suggested to explain the formation of the above products is similar to that offered to account for the isopropenylphenols arising from the condensations of allyl alcohol with phenols in the cold, under the influence of sulfuric acid. Fundamentally, it involves addition of the phenol to the double bond in the alcohol. Since the addition of anionoids to the ethylenic linkage cannot be a direct one, it is postulated that sulfuric acid first[6] adds to the unsaturation and this is eliminated in

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(1) From Part II of the thesis presented by Edward A. Storch to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy.

(2) Alexander, *Ber.*, **25**, 2409 (1892); Stoermer and co-workers, *ibid.*, **34**, 1810 (1901); **36**, 2873 (1903); Rindfusz and co-workers, THIS JOURNAL, **41**, 665 (1919); **42**, 157 (1920).

(3) Fries and Moskopp, *Ann.*, **372**, 195 (1910); Stoermer, Chydenius and Schinn, *Ber.*, **57**, 72 (1924); Claisen and co-workers, *ibid.*, **58**, 275 (1925); **59**, 2344 (1926); German Patent 279,864 (1914); Schering-Kahlbaum, British Patents 273,684–273,686 (1926); 306,051 (1927); Canadian Patent 278,726; 278,727 (1928); German Patent 501,723 (1926); U. S. Patent 1,679,664 (1928); 1,901,824 (1933).

(4) (a) Fries and Fickewirth, *Ann.*, **362**, 46 (1908); (b) Guillaumin, *Bull. soc. chim.*, [4] **7**, 381 (1910); (c) Niederl and co-workers, THIS JOURNAL, **53**, 3390 (1931); **55**, 284 (1933).

(5) Schering-Kahlbaum, Jordan, German Patent, 501,723 (1926).

(6) Robinson-Wreschner, "Versuch einer Elektronentheorie organisch-chemischer Reaktionen," F. Enke, Stuttgart, 1932, pp. 14–17.

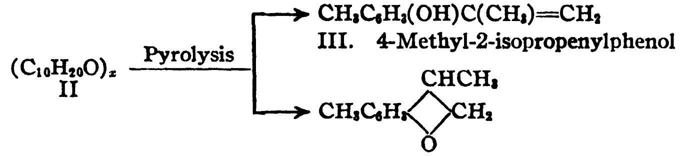
another sense, involving the phenolic group, to form an ether. Assuming alpha addition of the acid radical to have occurred (the structures of the final products rule out the possibility of beta addition), then the resulting ether would be β-(*p*-cresoxy)-propylene glycol (I).

Repulsion energy data compiled by Latimer[7] and application of these principles by the authors to a specific case, the isopropenyl aryl ethers, would indicate that ethers of the type I[8] possess a higher inner energy than the corresponding phenols and under the conditions of the present reaction readily undergo rearrangement. In the presence of sulfuric acid this transition is accompanied by the loss of water from the side chain. This loss may either precede or follow the rearrangement. In any case the resulting product, an alkali insoluble polymer with the empirical formula II, was isolated.

$$CH_2{=}CHCH_2OH + H_2SO_4 \longrightarrow HOCH_2(CH_3)CH\boxed{OSO_2OH + H}OC_6H_4CH_3 \longrightarrow$$

$$HOCH_2(CH_3)CHOC_6H_4CH_3 \xrightarrow[-H_2O]{\text{Rearrangement}}$$

I. β-(*p*-Cresoxy)-propyleneglycol



III. 4-Methyl-2-isopropenylphenol

IV. 2,4-Dimethylcoumarane

On distillation under ordinary pressures (slight decomposition took place), depolymerization was effected and the 2,4-dimethylcoumarane (IV) was isolated along with a small quantity of 4-methyl-2-isopropenylphenol (III).

In the condensation of allyl alcohol with *p*-cresol in the presence of sulfuric acid in the cold (0°), the resulting polymer was soluble in alkali. On distillation, the chief product was shown to be 4-methyl-2-isopropenylphenol (III). Therefore it was assumed that the solid condensation product was a polymer of the latter. In the present reaction, carried out at higher temperatures, the polymer differed from the above in that it was insoluble in alkali and on distillation gave rise chiefly to the 2,4-dimethylcoumarane (IV).

Allyl Alcohol–*m*-Cresol Condensation.—This system gave rise to a condensation product which appeared to be a polymer similar to the one discussed above. On pyrolytic decomposition, there was isolated 2,5-dimethylcoumarane and a small quantity of a phenolic product. The latter corresponded with the 5-methyl-2-isopropenylphenol,[4] while the former, the 2,5-dimethylcoumarane, was found to be identical with the product reported in the literature.[5]

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(7) Latimer, THIS JOURNAL, 51, 3185 (1929).

(8) Niederl and Storch, *ibid.*, 55, 284 (1933).

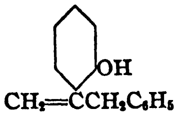
Allyl Alcohol–Phenol Condensation.—The reaction product was a polymer, which on distillation gave rise to a small quantity of a phenolic body and a greater yield of an alkali insoluble product which appeared to be 2-methylcoumarane. The alkali soluble product agreed in physical and chemical properties with *o*-isopropenylphenol,[9] yielding a crystalline bromine derivative which was identical with the hexabromo compound reported previously.[8]

Allyl Alcohol–*o*-Cresol Condensation.—The polymer resulting from this reaction was decomposed to yield an alkali insoluble product which represented the greater portion of the yield. It appeared to be 2,6-dimethylcoumarane. A very small quantity of a phenolic product was observed which appeared to correspond with the 6-methyl-2-isopropenylphenol known in the literature.[10]

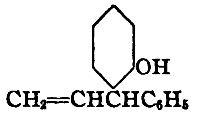
Arylated Coumaranes.—The work was extended to the aromatic series, involving the addition of various phenols to cinnamyl alcohol. In general the experimental procedure employed and the products isolated in the cinnamyl alcohol condensations resembled those obtained with allyl alcohol.

Cinnamyl Alcohol–Phenol Condensation.—The reaction of cinnamyl alcohol and phenol gave rise to a solid polymer which on distillation yielded chiefly an alkali-insoluble product. A small quantity of a phenolic body was observed in the distillate. The reaction appeared to be quite similar to the allyl alcohol–phenol condensations. Neither substance could be crystallized in a bath of solid carbon dioxide and acetone. Analyses of the products indicated that addition of the phenol to the unsaturation in the alcohol had taken place and that a molecule of water had been eliminated.

Assuming the reactions involving phenol formation to be identical with those leading to configuration IV (however, the possibility of beta addition to the ethylenic linkage must be considered as well as alpha addition), then the following structures might be suggested for the phenol isolated here.



V. 3-Phenyl-2-(2-hydroxy)phenylpropene-1
(Alpha addition)



VI. *o*-(α-Phenylallyl)phenol
(Beta addition)

The *o*-(α-phenyl allyl) phenol (VI) has been reported,[11] and possesses properties which differ from the phenol obtained in this research. It would appear, then, that the phenylisopropenylphenol (V) is the structure of the present product.

Further evidence for this structure may be obtained from a study of the alkali-insoluble heterocyclic compound. Assuming alpha addition of the phenol to the unsaturation in the alcohol, the polymer would pyrolyze to yield 2-benzylcoumarane (VII). In like manner, had beta addition been favored, then the resulting polymer might give rise to either a 4-phenylchromane (VIII) or a 1-methyl-2-phenylcoumarane (IX).

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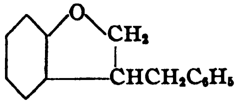
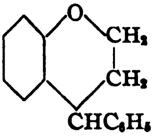
[9] (a) Béhal and Tiffeneau, *Bull. soc. chim.*, [4] **3**, 315 (1908); (b) Hoering and Baum, German Patent 208,886 (1909); (c) Fries and Volk, *Ann.*, **379**, 95 (1911).

[10] Béhal and Tiffeneau, *Bull. soc. chim.*, [4] **3**, 730 (1908).

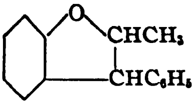
[11] Claisen and Tietze, *Ber.*, **58**, 275 (1925).



VII. 2-Benzylcoumarane



VIII. 4-Phenylchromane

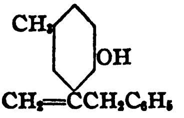


IX. 1-Methyl-2-phenylcoumarane

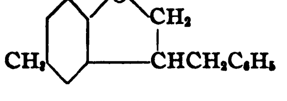
The latter two compounds have been prepared and characterized, the 4-phenylchromane (VIII) by Greenwood and Nierenstein,[12] and the 1-methyl-2-phenylcoumarane (IX) by Claisen and Tietze.[11] The compound obtained in this research did not agree with either of these and, therefore, appears to be the 2-benzylcoumarane (VII). Such a conclusion would indicate alpha addition of the phenol to the ethylenic linkage.

Cinnamyl Alcohol–*p*-Cresol Condensation.—On pyrolytic decomposition of the polymer resulting from the condensation of cinnamyl alcohol with *p*-cresol, two liquids, one phenolic in character (in small yield) and the other insoluble in alkali, were obtained. These products resembled in all respects the liquids isolated from the cinnamyl alcohol–phenol condensation.

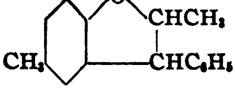
Presupposing alpha addition of the *p*-cresol to the ethylenic linkage in a manner similar to that previously described, then the phenolic product would be 3-phenyl-(2-hydroxy-5-methyl)-phenylpropene-1 (X) and the alkali-insoluble material would have the structure of 2-benzyl-4-methylcoumarane (XI). If beta addition had occurred, then the resulting phenolic product would be *o*-(α-phenylallyl)-*p*-cresol. This product has been reported in the literature[11] and differs in properties from the material obtained in this research. With respect to the major fraction obtained by distillation of the polymer, the coumarane structure, beta addition would lead to the formation of 1,4-dimethyl-2-phenylcoumarane (XII).



X. 3-Phenyl-(2-hydroxy-5-methyl)phenylpropene-1



XI. 4-Methyl-2-benzylcoumarane



XII. 1,4-Dimethyl-2-phenylcoumarane

A survey of the literature revealed that this product had not been previously prepared, but that it may be readily synthesized by the method of Claisen and Tietze.[11] The 1,4-dimethyl-2-phenylcoumarane (XII) was prepared and found to differ in physical and chemical properties from the substance obtained in this research. The former yielded a crystalline pentabromo derivative melting at 249°, whereas the latter by the same procedure gave rise to 2,3,5,6-tetrabromo-*p*-cresol.[13]

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[12] Greenwood and Nierenstein, *J. Chem. Soc.*, **117**, 1594 (1920).

Cinnamyl Alcohol–*m*-Cresol Condensation.—The condensations were extended to include the reaction of cinnamyl alcohol with *m*-cresol. The two products which were isolated were similar to those obtained in previous condensations. In view of the aforementioned proofs of structure and postulated reaction mechanisms the formation and configuration of the compounds isolated may be readily elucidated. The small quantity of phenolic material appeared to be a phenylisopropenyl-*m*-cresol and the major fraction, 2-benzyl-5-methylcoumarane.

Cinnamyl Alcohol–*o*-Cresol Condensation.—The reaction of cinnamyl alcohol with *o*-cresol was similar in all respects to the condensations previously discussed. The isolated products appeared to be a phenylisopropenyl-*o*-cresol, and 2-benzyl-6-methylcoumarane.

Experimental Part

The Condensation Method.[14]—To a solution of molar quantities of allyl (cinnamyl) alcohol and of the phenol (cresols) in 150 cc. of glacial acetic acid, a mixture of 10 cc. of concentrated sulfuric acid in 100 cc. of glacial acetic acid was added. The colorless solution was refluxed for five hours. During the course of the heating the reaction mixture took on a deep red coloration. After allowing to come to room temperature (preferably standing overnight), the solution was poured into excess cold water, the mixture being constantly stirred. With allyl alcohol condensations the reaction product appeared as a viscous oil, while with cinnamyl alcohol an amorphous precipitate was obtained. In any case the supernatant liquid was decanted. The polymerized condensation product was treated with 5% potassium hydroxide solution to remove any unreacted materials as well as traces of acid. It was washed repeatedly, first with hot water and then with cold water, until free from alkali. At this point the material was a solid. It was allowed to dry and then pulverized. The product distilled at ordinary pressure (very slight decomposition took place) as an orange-red liquid, a mixture of a phenol and coumarane. The distillate was collected over a range of 150–350°. The phenolic product, a small fraction of the total yield, was extracted from the mixture by means of a 20% potassium hydroxide solution and the coumarane layer separated. The coumarane, which represents the major portion of the yield (50–65% on the basis of the starting materials), was distilled under ordinary pressure. A small quantity of the phenolic product was obtained by acidification of the potassium hydroxide solution with concentrated hydrochloric acid. The colorless phenol was isolated by distillation of the oily layer under ordinary pressures.

Preparation of Bromine Derivatives.—These were prepared by treating the pure coumarane (or phenol) with an excess of bromine in the cold, without the use of a solvent. The whole was then allowed to stand until all the hydrogen bromide and excess bromine had evaporated. The dark mass was transferred to a porous tile and washed

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(13) Bodroux, *Compt. rend.*, **126**, 1283 (1898); Zincke and Buff, *Ann.*, **341**, 327 (1905); Wiederhold, *Ann.*, **320**, 206 (1902); Auwers, *Ber.*, **35**, 464 (1902); Hantzsch and Scholtze, *Ber.*, **40**, 4882 (1907).

(14) Niederl and co-workers, THIS JOURNAL, **50**, 2230 (1928); **51**, 2426 (1929); **53**, 272, 806, 1928, 3390 (1931); **54**, 1063 (1932); **55**, 284, 2571, 3025 (1933); *Monatsh.*, **51**, 1028 (1929); **60**, 150 (1932); *Z. angew. Chem.*, **44**, 467 (1931); **46**, 396 (1933).

successively with small quantities of carbon tetrachloride to remove the tarry material and last traces of bromine. Recrystallizations were then effected from carbon tetrachloride.

Acknowledgment is made here to Miss Roslyn T. Roth of this Laboratory for performing the many quantitative micro-analytical determinations.

TABLE I

ALLYL ALCOHOL–PHENOL CONDENSATIONS

	Compound	With ferric chloride in alcoholic solution	M. p., °C.	B. p., °C.
	Products with Phenol			
1	*o*-Isopropenylphenol[8,9,10]	Brown		202–205 (60–62, 5 mm.)
2	Hexabromo-*o*-isopropylphenol[8]		85–86	
3	2-Methylcoumarane			208–212
	Products with *p*-Cresol			
4	4-Methyl-2-isopropenylphenol[4]	Violet, changing to brown		218–222
5	2,4-Dimethylcoumarane[5]			228–232 (103, 11 mm.)
	Products with *m*-Cresol			
6	5-Methyl-2-isopropenylphenol[9,9,10]	Green, changing to brown		220–224
7	2,5-Dimethylcoumarane[5]			250–255 (99–100, 11.5 mm.)
	Products with *o*-Cresol			
8	6-Methyl-2-isopropenylphenol[9a]	Green		212–216
9	Pentabromo-6-methyl-2-isopropylphenol		190–191	
10	2,6-Dimethylcoumarane			253–258

	Formula	Sp. gr.	n_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	$CH_2{=}C(CH_3)C_6H_4OH$		1.5414 (24°)				
2	$C_9H_6OBr_6$						
3	$C_9H_{10}O$	1.028 (25°)	1.5302 (25°)	80.59	80.20	7.46	7.68
4	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		1.5380 (24°)				
5	$C_{10}H_{12}O$	1.000 (25°)	1.5281 (25°)	81.08	81.40	8.10	8.20
6	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$		1.5399 (23°)				
7	$C_{10}H_{12}O$	1.007 (23°)	1.5364 (23°)	81.08	81.45	8.10	8.27
8	$CH_2{=}C(CH_3)C_6H_3(CH_3)OH$	1.012 (25°)	1.5390 (25°)				
9	$C_{10}H_9OBr_5$			22.01	22.32	1.65	1.32
10	$C_{10}H_{12}O$	0.993 (25°)	1.5289 (25°)	81.08	81.35	8.10	8.32

TABLE II

CINNAMYL ALCOHOL–PHENOL CONDENSATIONS

	Compound	With ferric chloride in alcoholic solution	M. p., °C.	B. p., °C.
	Products with Phenol			
1	3-Phenyl-2-(2-hydroxy)-phenylpropene-1	Brown		193–196
2	2-Benzylcoumarane			308–311
	Products with *p*-Cresol			
3	3-Phenyl-2-(2-hydroxy-5-methyl)-phenylpropene-1	Green		208–212
4	2-Benzyl-4-methylcoumarane		198–199	320–325
5	2,3,5,6-Tetrabromo-*p*-cresol[13]			
6	1,4-Dimethyl-2-phenylcoumarane[11,a]		249	310–314
7	Pentabromo-1,4-dimethyl-2-phenylcoumarane			
	Products with *m*-Cresol			
8	3-Phenyl-2-(2-hydroxy-4-methyl)-phenylpropene-1	Green, slowly changing to brown		207–211
9	2-Benzyl-5-methylcoumarane			322–327
	Products with *o*-Cresol			
10	3-Phenyl-2-(2-hydroxy-3-methyl)-phenylpropene-1	Brown		212–216
11	2-Benzyl-6-methylcoumarane			318–322

TABLE II (*Concluded*)

	Formula	Sp. gr.	n_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	$CH_2=C(HOC_6H_4)CH_2C_6H_5$	0.953 (25°)	1.5027 (25°)	85.71	85.37	6.66	6.43
2	$C_{15}H_{14}O$	1.061 (25°)	1.5760 (25°)	85.71	85.46	6.66	6.46
3	$CH_2=C(HOC_6H_3CH_3)CH_2C_6H_5$	1.000 (27°)	1.5314 (27°)	85.71	85.40	7.14	7.36
4	$C_{16}H_{16}O$	1.047 (26°)	1.5778 (26°)	85.71	86.03	7.14	7.53
5	$C_7H_4OBr_4$			19.81	20.32	0.94	0.98
6	$C_{16}H_{16}O$	1.080 (29°)	1.5671 (29°)				
7	$C_{16}H_{11}OBr_5$			31.02	31.39	1.77	1.52
8	$CH_2=C(HOC_6H_3CH_3)CH_2C_6H_5$	1.033 (24°)	1.5299 (24°)	85.71	85.75	7.14	7.15
9	$C_{16}H_{16}O$	1.080 (24°)	1.5836 (24°)	85.71	85.38	7.14	7.08
10	$CH_2=C(HOC_6H_3CH_3)CH_2C_6H_5$	0.993 (21°)	1.5352 (21°)	85.71	85.56	7.14	7.54
11	$C_{16}H_{16}O$	1.047 (21°)	1.5860 (21°)	85.71	85.40	7.14	7.15

[a] This compound was prepared by P. F. Geller and M. Rothstein in conjunction with research work for the Master of Science degree at New York University.

Summary

1. Further studies in the addition reaction of phenols to unsaturated alcohols (allyl alcohol in the aliphatic and cinnamyl alcohol in the aromatic series) have shown that by altering experimental conditions, coumaranes can be obtained.

2. Under the new conditions (elevated temperature and solvent), the chief products were shown to be methylated coumaranes (with allyl alcohol), benzyl and methylbenzyl substituted coumaranes (with cinnamyl alcohol). This affords a new and convenient method for the synthesis of alkyl and aryl substituted benzodihydrofurans.

3. Further work is now in progress extending these studies to polyhydroxy phenols and other unsaturated alcohols (crotyl-, oleyl alcohols) under various reaction conditions.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Preparation and Reactions of 4,4-Dimethylpentene-1 (Neopentylethylene)

BY FRANK C. WHITMORE AND AUGUST H. HOMEYER[1]

The peculiar effects of the presence of a neopentyl system on the nature of a variety of compounds have been studied extensively in this Laboratory.[2] 4,4-Dimethylpentene-1 was synthesized from *tert*-butylmagnesium chloride and allyl bromide. Addition of hydrogen bromide gave only the primary bromide, 1-bromo-4,4-dimethylpentane. This appears to be the first case in which complete reversal of Markownikoff's Rule[3] has been observed in an aliphatic olefinic hydrocarbon. This anomalous behavior is

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(1) Mallinckrodt Research Fellow.

(2) Whitmore and co-workers, THIS JOURNAL, 1932–1933.

(3) Markownikoff, *Ann.*, **153**, 256 (1870).

doubtless attributable to the nature of the neopentyl group and recalls the action of benzylethylene[4] and acrylic acid to yield primary halides by addition. 4,4-Dimethylpentene-1 failed to react with dry hydrogen iodide at 0–5°.[5] Reaction with acetic acid in the presence of sulfuric acid gave the acetate of 4,4-dimethylpentanol-2 and a mixture of olefins. 4,4-Dimethylpentene-1 forms a dibromide from which the original olefin can be regenerated without rearrangement.

1-Bromo-4,4-dimethylpentane was converted to the corresponding alcohol by treatment of the Grignard reagent with oxygen.

Several of the preparations have been checked by W. R. Trent of this Laboratory.

Experimental

4,4-Dimethylpentene-1.—Five moles (605 g.) of allyl bromide, b. p. 68.8–69.3° (738 mm.), diluted with 500 cc. of dry ether was placed in a 5-liter 3-necked flask fitted with a mercury-sealed stirrer, a thermometer and a graduated separatory funnel of 1-liter capacity. The flask was cooled in a large bath of ice and salt at about −10° while 5.2 moles (2400 cc.) of carefully filtered *tert*-butylmagnesium chloride solution was added from the funnel during sixteen hours with the temperature of the reaction mixture below 5°. The coupling reaction took place with the evolution of heat and the separation of white magnesium halide. After stirring for several hours at room temperature the presence of excess Grignard reagent was verified by the color test of Gilman and Schulze[6] using a 5-cc. sample. The product was poured on ice. The voluminous solid magnesium halide etherate was broken up and decomposed with ice and ammonium sulfate. The ether layer was separated. The aqueous layer was steam distilled and the upper layer of the distillate was added to the main portion. The ether solution was washed with ammoniacal ammonium sulfate solution to remove magnesium salts, dried over 100 g. of calcium chloride and fractionated through an 85 × 2.1 cm. packed column of the total condensation, adjustable take-off type.[7] An efficient spiral condenser was used and the receiver was cooled in ice. After removing the ether, intermediate fractions were collected amounting to 159 g., b. p. 36–70.7°. Then 315 g. of 4,4-dimethylpentene-1 distilled at 70.7–71.2° (724 mm.), n^{20}_{D} 1.3918. The intermediate fractions were refractionated, yielding 105 g. more of the olefin.

Fraction	B. p., °C.	(Mm.)	n^{20}_{D}	Wt., g.
1-2	36–46	(724)	1.3528–1.3571	32
3-4	46–68		1.3810–1.3876	11
5-7	68–70.8		1.3902–1.3920	105
8-9	70.7–71.2		1.3918	315
10	Residue		Black oil	37

The yield (fractions 5–9) was 420 g. or 85% of the theoretical based on allyl bromide. The various fractions gave a slight Beilstein test for halogen and the index of

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(4) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928). Since this paper was completed interesting work by Kharasch and co-workers on the effect of peroxide on addition to olefins has appeared [THIS JOURNAL, **55**, 2468, 2521 (1933)]. The effect of peroxides and antioxidants on addition reactions of neopentylethylene is being studied in this Laboratory. Also Sherrill and co-workers have found that pentene-1 and heptene-1 with gaseous hydrogen bromide give exclusively the primary bromide (Organic Division, American Chemical Society Meeting, Chicago, September, 1933).

(5) Unpublished results by W. R. Trent of this Laboratory.

(6) Gilman and Schulze, *Bull. soc. chim.*, [4] **41**, 1479 (1927); THIS JOURNAL, **47**, 2002 (1925).

(7) Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

refraction was a little higher than for the olefin purified through the dibromide. The low index of fractions 3–4 shows the absence of diallyl,[8] b. p. 59.6° (760 mm.), n_D^{20} 1.4044.

In a preliminary experiment it was found that the addition of allyl bromide diluted with ether to the *tert*-butylmagnesium chloride solution at 2° resulted in a four-fold increase in the high-boiling residue. Fractionation of the residue (160 g.) from a 5-mole run showed it to consist of polymers, and 23.5 g. of solid hexamethylethane, b. p. 101–109°, was isolated. In this case, and also when the Grignard reagent was added to the diluted allyl bromide without cooling, diallyl was isolated from the fore-runs as the tetrabromide, m. p. 52°, after crystallizing from alcohol and then from a mixture of ether and petroleum ether.

1,2-Dibromo-4,4-dimethylpentane.—The dibromide was prepared by adding dry bromine to a dilute ether solution of the olefin at −5°. The yield was 85%; b. p. 77–78° (9 mm.), n_D^{20} 1.4970, d_4^{20} 1.5129; MR found 49.89, calcd. 50.05.

4,4-Dimethylpentene-1 from its Dibromide.—Sixty-five grams of zinc dust and 260 cc. of 95% alcohol were placed in a 1-liter 3-necked flask fitted with a reflux condenser, mercury-sealed stirrer and dropping funnel. To the boiling mixture was added 192 g. of 1,2-dibromo-4,4-dimethylpentane from the dropping funnel during one and one-half hours. The product was distilled through a 91 × 1.4 cm. packed column. One hundred fifty cc. of distillate was collected at 59–78°. This was diluted with 400 cc. of water; the olefin layer was separated, washed with 250-cc. and 100-cc. portions of water, dried over 3 g. of calcium chloride and fractionated through a 91 × 1.4 cm. packed column. Forty-five grams (91%) of 4,4-dimethylpentene-1 distilled at 71.8° (730 mm.). There were no by-products and the product was free from halogen. 4,4-Dimethylpentene-1 has the following properties: b. p. 72.35° (760 mm.) (Cottrell); n_D^{20} 1.3911; d_4^{20} 0.6827; d_0^0 0.7007; MR found 34.15 (Lorentz–Lorenz), calcd. 34.06 (Eisenlohr).

Ozonolysis.—Several 0.5-mole quantities of 4,4-dimethylpentene-1 were ozonized.[9] The yield of ozonide was 85–91%. Decomposition gave both *tert*-butylacetaldehyde (40–45%) and *tert*-butylacetic acid (40%). Formaldehyde was identified by the resorcinol–sulfuric acid test. *tert*-Butylacetic acid was identified as the amide,[10] m. p. 132°.

tert-Butylacetaldehyde distilled at 102–104° (730 mm.); 2,4-dinitrophenylhydrazone, m. p. 146–147°. A mixture with acetaldehyde-2,4-dinitrophenylhydrazone, m. p. 147°, melted at 127–130°. *tert*-Butylacetaldehyde condensed with dimethyldihydroresorcinol[11] in alcoholic solution yielding a product melting at 167° after recrystallization from 70% alcohol.

3,3-Dimethylbutanol-1 was obtained by reduction of *tert*-butylacetaldehyde with an Adams catalyst. It distilled at 139–140° (727 mm.); Delacre[12] gives 142.6–143.6°. Its α-naphthyl urethan melts at 83°.

1-Bromo-4,4-dimethylpentane.—Fifty grams of 4,4-dimethylpentene-1 was saturated with dry hydrogen bromide at 0°. After keeping at 5° for eighteen hours, the bromide was refluxed under a 70 × 1 cm. indented column at 50 mm. to remove excess hydrogen bromide. A little anhydrous potassium carbonate was added and the bromide was fractionated. Seven fractions were collected; all had identical physical properties: b. p. 70–71° (35 mm.), 154° (730 mm.); n_D^{20} 1.4484; d_4^{20} 1.1343; MR found, 42.29, calcd. 42.29. The yield was 78 g. or 88%.

No hydrolysis could be detected after shaking a sample with water for thirty minutes. Shaking for three hours with 0.1 *N* silver nitrate gave 4.4% hydrolysis. It forms a Grignard reagent which reacts with mercuric bromide[13] to give 1-bromomercuri-4,4-dimethylpentane, m. p. 101°, after crystallization from 95% alcohol.

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[8] Cortese, THIS JOURNAL, 51, 2266 (1929).

[9] Whitmore and Church, *ibid.*, 54, 3710 (1932).

[10] Homeyer, Whitmore and Wallingford, *ibid.*, 55, 4211 (1933).

[11] Weinberger, *Ind. Eng. Chem., Anal. Ed.*, 3, 365 (1931).

[12] Delacre, *Bull. sci. acad. roy. Belg.*, 7–41 (1906); *Chem. Zentr.*, I, 1283 (1906).

After passing dry hydrogen iodide through 0.5 mole of 4,4-dimethylpentene-1 for twenty-four hours at 0–5° there was no gain in weight. The olefin was recovered unchanged.[5]

4,4-Dimethylpentanol-1.—1-Bromo-4,4-dimethylpentane was converted to the Grignard reagent in the usual manner; yield 82% in a 0.5-mole run.

A solution of 0.14 mole of the Grignard reagent was cooled and treated with dry oxygen. The product was poured over ice and ammonium chloride; the ether layer was separated and the aqueous layer was extracted with 100 cc. of ether, the extract being added to the main portion. After drying over potassium carbonate the product was fractionated through a 55 × 1.2 cm. indented column. Fifteen grams (90% yield based on the Grignard reagent) of 4,4-dimethylpentanol-1 was obtained: b. p. 96° (62 mm.), 158° (737 mm.); n^{20}_{D} 1.4202; d^{20}_{4} 0.815; MR found 36.07, calcd. 36.17.

The α-naphthyl urethan of 4,4-dimethylpentanol-1 melts at 80.5–81° after crystallizing from petroleum ether. 4,4-Dimethylpentanol-2[14] boils at 137.5° (736 mm.) and its α-naphthyl urethan melts at 86.5–87°. A mixture melted at 60–65°.

The structure of 4,4-dimethylpentanol-1 was further established by oxidation with chromic acid yielding neopentylacetic acid, b. p. 198–208°; amide m. p. 141–142° after crystallization from water. Moureu and Delange[15] give 140–141°.

Addition of Acetic Acid to 4,4-Dimethylpentene-1.—Five cc. of 100% sulfuric acid (m. p. 8°), 150 cc. of glacial acetic acid (m. p. 16.6°) and 50 g. of 4,4-dimethylpentene-1 were heated on the steam-bath for two days. The solution became dark. The product was poured over ice and diluted with twice its volume of water. The dark upper layer was separated, washed with dilute sodium bicarbonate solution and dried over potassium carbonate. It weighed 46 g. Fractionation through a 70 × 1 cm. indented column gave 13 fractions. Fractions 1–6, 18 g. (36%), b. p. 72–82° (740 mm.), n^{20}_{D} 1.3960–1.4000. This mixture of heptenes was not investigated further.

Fractions 7–13, 26 g. (33%): b. p. 92° (90 mm.), 154° (735 mm.); n^{20}_{D} 1.4080; d^{20}_{4} 0.858. These properties agree with the properties of a known sample of the acetate of 4,4-dimethylpentanol-2:[14] b. p. 92–93° (90 mm.); n^{20}_{D} 1.4071; d^{20}_{4} 0.8563.

Twenty grams of the ester (fractions 8–12) was hydrolyzed by warming for two days with 15 g. of potassium hydroxide dissolved in 85 cc. of 80% alcohol. The product was diluted with three times its volume of water; the upper layer was separated, washed with water, dried over copper sulfate and fractionated through a 70 × 1 cm. indented column. Four fractions were obtained weighing 14 g.: b. p. 136–137° (741 mm.); n^{20}_{D} 1.4185–1.4190; d^{20}_{4} 0.812. These properties agree with those of a known sample of 4,4-dimethylpentanol-2: b. p. 137–137.5° (736 mm.); n^{20}_{D} 1.4188; d^{20}_{4} 0.8115. Its α-naphthyl urethan melted at 85–85.5°. The α-naphthyl urethan of a known sample of 4,4-dimethylpentanol-2 melted at 86.5–87° and a mixture melted at 85.8–86.4°.

Action of Sulfuric Acid on 4,4-Dimethylpentene-1.—Fifty grams of 4,4-dimethylpentene-1 was added with shaking to 156 g. of 85% sulfuric acid cooled to 5°. The temperature rose to 20°. The product was poured over ice; the upper layer was separated, washed with sodium bicarbonate solution, dried over potassium carbonate and fractionated through a 70 × 1 cm. indented column. The product was a mixture of polymers weighing 45 g.: b. p. 59° (13 mm.) to 122° (11 mm.), n^{20}_{D} 1.4309–1.4502.

Refluxing samples of 4,4-dimethylpentene-1 with 5% by volume of 100% sulfuric acid or small amounts of dilute sulfuric acid for one hour caused no appreciable change in the boiling point or index of refraction of the olefin. The strong acid caused some charring.

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(13) Marvel, Gauerke and Hill, THIS JOURNAL, 47, 3009 (1925).

(14) Whitmore and Homeyer, *ibid.*, 55, 4195 (1933).

(15) Moureu and Delange, *Bull. soc. chim.*, [3] 29, 665 (1903).

Summary

4,4-Dimethylpentene-1 has been prepared from allyl bromide and *tert*-butylmagnesium chloride, and purified through its dibromide. Addition of hydrogen bromide takes place contrary to Markownikoff's rule, giving 1-bromo-4,4-dimethylpentane exclusively. The latter has been converted to 4,4-dimethylpentanol-1 through the Grignard reaction. 4,4-Dimethylpentene-1 does not add dry hydrogen iodide at 0–5°; it reacts with acetic acid in the presence of sulfuric acid yielding the acetate of 4,4-dimethylpentanol-2 and a mixture of olefins.

STATE COLLEGE, PENNSYLVANIA

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Hydrogenolysis of Sugars

BY WALTER H. ZARTMAN AND HOMER ADKINS

Since certain types of glycols undergo cleavage at carbon to oxygen or carbon to carbon linkages when submitted to the action of hydrogen over a suitable catalyst, it seemed of interest to ascertain the facts with regard to the behavior of the sugars under these conditions. The experimental results of this study of the hydrogenolysis of the more common sugars may, perhaps, be most concisely and clearly presented by first giving a description of the experimental procedure and observations with respect to sucrose.

A rapid reaction ensued when 171 g. (0.5 mole) of sucrose in 175 ml. of dry ethanol with 20 g. of copper–chromium oxide at 250° was subjected to the action of hydrogen under a pressure of about 300 atmospheres.[1] During the course of two or three hours about 4.7 moles of hydrogen was absorbed, whereupon the reaction apparently stopped. After centrifuging out the catalyst the perfectly colorless reaction mixture was fractionated through an electrically heated Widmer column, having a spiral 20 cm. in length. Alcohol and water were distilled at atmospheric pressure. Fractionation of the remainder at 7 mm. resulted in a distillation curve similar to that marked "A" in Fig. 1. There was apparently a large amount of a compound boiling at about 80° (7 mm.), a very small amount at about 138° (7 mm.), a larger fraction at about 175° (7 mm.), with 22 g. of higher boiling material.

The fraction collected at atmospheric pressure was obviously largely composed of the ethanol originally used as the solvent. Analysis of it by the method of Wright showed that it contained about 4 g. of methanol.[2]

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[1] The catalyst and apparatus has been described by Connor, Folkers and Adkins, THIS JOURNAL, 54, 1140 (1932), and Adkins, *Ind. Eng. Chem., Anal. Ed.*, 4, 342 (1932); see also Connor and Adkins, THIS JOURNAL, 54, 4678 (1932), on hydrogenolysis of glycols.

[2] Wright, *Ind. Eng. Chem.*, 19, 750 (1927).

Calculations based upon the amount and density of the fraction showed that it contained about 24 g. of water and 13 g. of ethanol, resulting from the hydrogenolysis of the sucrose. The fraction boiling at 78–83° (7 mm.) was readily identified as propanediol-1,2. The higher boiling fractions were too small in amount for their purification and identification from a single hydrogenolysis. However, the careful fractionation at 1 mm. of the material boiling above 83° (7 mm.) from several reaction mixtures gave three fractions: I, b. p. 118–125°; II, b. p. 142–144°; and III, b. p. 214–215°. The analysis of I showed its formula to be $C_6H_{12}O_3$, the analysis of II showed $C_6H_{14}O_3$, while III was found to be $C_6H_{14}O_4$. The molecular refractions of these compounds as well as other data showed I to be a dihydroxy ether, II a trihydric alcohol, and III a tetrahydric alcohol. The tentative structural formulas suggested for these compounds are, respectively

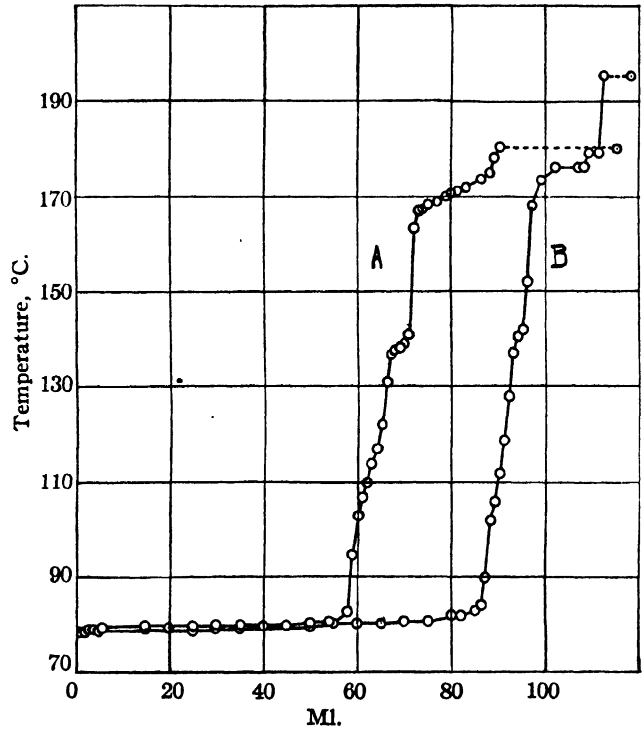
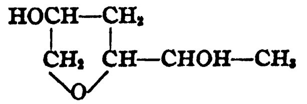


Fig. 1.—Distillation curves of products boiling above 78° (7 mm.) from lactose (A) and mannitol (B).



2-(4-Hydroxytetrahydrofuryl)-methylcarbinol
I

$CH_2OHCHOHCH_2CH_2CHOHCH_3$
Hexanetriol-1,2,5
II

$CH_2OHCHOHCH_2CH_2CHOHCH_2OH$
Hexanetetrol-1,2,5,6
III

TABLE I

HYDROGENOLYSIS OF SUGARS

Moles sugar	and	H_2	CH_3OH, g.	C_2H_5OH, g.	H_2O, g.	C_3H_6-$(OH)_2$, g.	$C_6H_{10}O$-$(OH)_2$, g.	C_6H_{11}-$(OH)_3$, g.	C_6H_{10}-$(OH)_4$, g.	Residue, g.
1.0	Glucose	4.9	6	10	25	91	6	13	..	17
1.0	Sorbitol	4.2	6	14	18	93	6	9	12	Trace
1.0	Mannitol	4.2	4	15	27	90	4	17	5	5
0.5	Sucrose	4.7	4	13	24	54	11	16	11	22
0.5	Lactose	4.6	4	19	23	54	7	20	9	23
0.5	Maltose	4.6	5	14	32	59	5	17	..	32
0.7	α-Methyl-*d*-glucoside	3.1	6	6	22	20	6	12	10	3
0.3	Pentacetylglucose	3.9	1	..	19	6	12	3	..	5
1.0	Gluconic lactone	4.8	2	15	29	16	15	(6 g. $C_2H_4(OH)_2$)		55

The assignment of positions to the various hydroxyl groups is based principally upon the following considerations. First, no two hydroxyls may be in the 1,3 or β position with respect to each other, for hydroxyl groups in such positions are very unstable over copper–chromium oxide at 250° under high pressures of hydrogen. This statement is based upon observations on the behavior of many 1,3 glycols in this Laboratory by Folkers, Connor, Wojcik, Sprague and others. The presence of a CH_3-CHOH group in I and II and the absence of such a group in III was shown by the iodoform test. These facts in the case of compounds I and III can apparently only be reconciled by the formulas given above. Compound II might have the 1,4,5 rather than the 1,2,5 structure but the latter is preferable on account of its closer relationship to I and III, and because the hydroxyls in the 3 and 4 positions should be eliminated first on hydrogenolysis since each of them has two hydroxyls in the β position with respect to it.

There is given in Table I a summary of the data on the absorption of hydrogen, and the weight of the various products obtained from glucose, sorbitol, mannitol, sucrose, lactose, maltose, α-methyl-*d*-glucoside, pentacetylglucose, and gluconic lactone under the conditions described above for sucrose.[3,4] The data given on the true sugars and for gluconic lactone are the averages of two or more duplicate experiments, those on the other four compounds represent single experiments. In no case was there any material variation on duplicate experiments. For the purpose of tabulation the material boiling over the range 78–83° (7 mm.) is listed as $C_3H_8O_2$, 130–145° (7 mm.) as $C_6H_{12}O_3$, and 165–180° (7 mm.) as $C_6H_{14}O_3$. The material listed as "residue" contained no appreciable amounts of unchanged sugar but was largely $C_6H_{14}O_4$. The yields of the higher boiling products are materially increased by interrupting the hydrogenolysis after the absorption of 2 or 3 moles of hydrogen.

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(3) The materials used in this investigation were commercially available or were prepared by standard methods.

(4) The hydrogenation of mannitol, glucose, sucrose and similar compounds over a metal of the platinum or iron group is claimed: I. G. Farbenind., German patent 541,326 (1927); *Chem. Abst.*, **26**, 1939 (1932); French Patent 662,874 (1928), *Chem. Abst.*, **24**, 378 (1930).

There is a close similarity in the behavior toward hydrogenolysis of glucose, sorbitol, mannitol, sucrose, maltose and lactose. The disaccharides took up 4.6 to 4.7 moles of hydrogen per 0.5 mole of sugar but there was a considerable "residue" after distillation of the products. The equivalent amount of glucose (1.0 mole) took up 4.9 moles of hydrogen with a less "residue" than the disaccharides. The hexahydric alcohols took up 4.2 moles of hydrogen with very small residues. Since 1 mole of hydrogen had already been taken up by these alcohols in the course of their preparation from the hexoses, it would thus appear that one mole of the simple sugar or the equivalent 0.5 mole of the disaccharide would take up about 5.3 moles of hydrogen. The statement that reaction apparently stopped after the absorption of about 5 moles of hydrogen per mole of monosaccharide should not be taken to mean that the glycols obtained would not undergo further hydrogenolysis at 250° under 300 atmospheres of hydrogen over copper–chromium oxide. In fact, some of the "residues" were converted into the lower boiling products previously isolated when again subjected to the action of hydrogen. The elimination of hydroxyl groups from the glycols therefore occurs but the reaction is very slow as compared to the hydrogenolysis of the sugars themselves. It appears that a rapid hydrogenolysis of the sugars occurs with the absorption of a little over 5 moles of hydrogen per mole of monosaccharide and that the rate of the reaction then changes very markedly.

There is one very marked difference between the three disaccharides and glucose (or the hexahydric alcohols) which is brought out by a comparison of the distillation curves for the products from lactose and mannitol as given in Fig. 1. The yield of propanediol-1,2 from the latter group is more than 60% greater than that from the former. This difference in yields of the glycol shows that the first step in the hydrogenolysis of the disaccharides is not the cleavage of the disaccharide to monosaccharides or the corresponding hexahydric alcohols.

The yields of propanediol-1,2 from *α*-methyl-*d*-glucoside and pentacetylglucose were quite low as compared with that from the parent sugar.

PROPERTIES AND ANALYSES OF PRODUCTS

No.	Compound	B. p., °C. (1 mm.)	d^{25}_{25}	n^{25}_{D}	MR_D Calcd.	MR_D Found
1	2-(4-Hydroxytetrahydrofuryl)-methylcarbinol	118–125	1.1452	1.4752	32.40	32.48
2	Hexanetriol-1,2,5	142–144	1.1075	1.4732	34.32	33.97
3	Hexanetetrol-1,2,5,6	214–215	....	....	...	...

No.	Formula	Analyses, % Carbon Calcd.	Carbon Found		Hydrogen Calcd.	Hydrogen Found	
1	$C_6H_{12}O_3$	54.50	54.89	54.83	9.10	9.29	9.29
2	$C_6H_{14}O_3$	53.70	53.19	53.32	10.44	10.41	10.43
3	$C_6H_{14}O_4$	48.00	48.20	48.00	9.33	9.39	9.34

Gluconic lactone was the only one of the derivatives of the sugars submitted to hydrogenolysis which did not react smoothly. A large amount of non-volatile tarry material was obtained. Noteworthy was the formation of ethylene glycol from this lactone as well as a relatively high yield of the 2-(4-hydroxytetrahydrofuryl)-methylcarbinol. The formation of this latter compound is not surprising since gluconic lactone contains the same ring structure as does the tetrahydrofuran derivative represented in Formula I.

Summary

Glucose, sorbitol, mannitol, sucrose, lactose, maltose, α-methyl-*d*-glucoside, pentacetylglucose and gluconic lactone in ethanol solution have been submitted to the action of hydrogen under 300 atmospheres at 250° in the presence of a copper–chromium oxide catalyst. All of the compounds under these conditions undergo a rapid hydrogenolysis to methanol, ethanol, propanediol-1,2 and three additional hydroxy compounds to which the following tentative formulas have been assigned, 2-(4-hydroxytetrahydrofuryl)-methylcarbinol, hexanetriol and hexanetetrol. No attempt is made to formulate the series of reactions involved in the formation of these products because, in our opinion, there is no conclusive evidence on the basis of which a choice may be made between several alternatives. However, the formation of each of the products is understandable in consideration of the behavior toward hydrogenolysis of simpler glycols, aldehydes and ketones which are being studied in this Laboratory.

MADISON, WISCONSIN RECEIVED JUNE 12, 1933
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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Action of Carbon Monoxide on Iron and Cobalt Complexes of Cysteine

BY MAXWELL P. SCHUBERT

I. Introduction.—In continuation of studies of the iron and cobalt complexes of thiol acids, the reaction of carbon monoxide with these compounds has been taken up. Cremer[1] was the first to observe that solutions of ferrous and cobaltous complexes of cysteine absorb carbon monoxide and from a study of the maximum amount absorbed and the proportion of metal to cysteine under which this takes place, concluded that there must exist in solution the complexes Fe(cysteine)$_2$(CO)$_2$ and Co(cysteine)$_2$(CO). The concern of the present paper is the actual isolation of the complexes which occur in solutions of ferrous and of cobaltous biscysteinate after they have absorbed carbon monoxide.

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(1) W. Cremer, *Biochem. Z.*, **206**, 228 (1929).

II. The Ferro Biscysteinate Dicarbonyl Complex.—A solution of potassium ferro biscysteinate, whose isolation has been described previously,[2] was made by mixing the components in the proportions of two moles of cysteine hydrochloride, one mole of ferrous salt and six moles of potassium hydroxide. This amount of alkali is just equivalent to the sum of the iron and acid. Such a solution made in an atmosphere of carbon monoxide absorbs two moles of the gas in two to four hours after which there is no further absorption. The data need not be given as they agree with those of Cremer. Even with double this proportion of alkali the total amount of carbon monoxide absorbed does not change though the rate of absorption is lower. This behavior differs markedly from that of the cobalto biscysteinate complex as will be shown later.

The complex can easily be prepared from its components provided oxygen be carefully excluded during its formation. For this purpose a special flask was constructed. A 250-cc. Erlenmeyer flask is fitted with a side arm having a glass stopcock. Into the neck of the flask is ground a glass stopper carrying a gas inlet tube also fitted with a glass stopcock and a small dropping funnel. In the flask are placed 3.9 g. of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, 3.2 g. of cysteine hydrochloride and 20 cc. of water. The air is swept out with hydrogen freed of oxygen by passage over heated copper. The test described by Von Wartenberg,[3] the disappearance of the phosphorus halo, is used to show when oxygen has been removed. Then 8 cc. of 6.5 *M* potassium hydroxide is admitted through the dropping funnel and the orange color of the ferro biscysteinate complex appears. A stream of carbon monoxide, generated from formic and sulfuric acids and washed with alkaline pyrogallol, is passed through the flask while the mixture is shaken steadily for four hours. The color appears to deepen during this process. Ten cc. of concentrated hydrochloric acid is added, the mixture shaken and set on ice. Precautions against admission of oxygen are no longer necessary as the carbon monoxide complex is stable in air. The mixture rapidly becomes solid with masses of yellow needles. These are filtered off, washed with a little ice cold water and alcohol and dried in a desiccator over sulfuric acid at 1 mm. There is no tendency for carbon dioxide to dissociate in a vacuum as determined by analysis after leaving *in vacuo* for various periods of time.

Anal. Calcd. for $Fe(SCH_2CHNH_2COOH)_2 \cdot 2CO \cdot H_2O$: Fe, 15.13; S, 17.29; N, 7.57; C, 25.94; H, 3.82. Found: Fe, 15.49; S, 17.28; N, 7.70; C, 26.15; H, 3.86.

The sodium salt can be prepared using sodium hydroxide in place of potassium hydroxide and of course omitting the addition of acid. On cooling in an ice-box overnight fine needles separate. After separating, washing and drying in a vacuum they show the following analysis.

Anal. Calcd. for $Fe(SCH_2CHNH_2COONa)_2 \cdot 2CO \cdot 2H_2O$: Fe, 12.96; S, 14.81; Na, 10.65; C, 22.21; H, 3.27. Found: Fe, 13.32; S, 15.18; Na, 10.61; C, 22.08; H, 3.93.

These experiments were carried out in diffuse daylight and it made no apparent difference in the amount of carbon monoxide absorbed whether the contents of the flask were protected from such light or not. This need not contradict Cremer's observation that the complex dissociates carbon monoxide on illumination as no experiments were carried out under intense illumination. Both of these compounds are quite stable in air when dry, the free acid decomposes in solution, within a few days at ice temperature and within an hour on warming. This decomposition is simply a dissociation, the total carbon monoxide being liberated as such and the ferro biscysteinate complex breaking up to ferrous salt and cysteine. As for the structure of this complex there seems to be no reason at present for supposing it other than the same as potassium ferro biscysteinate[2] with two carbonyl groups held by coördinate links directly to the iron:

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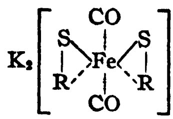
(2) Schubert, THIS JOURNAL, 54, 4077 (1932).

(3) H. Von Wartenberg, *Z. Elektrochem.*, 36, 295 (1930).



where R = $—CH_2CHNH_2COO—$

III. The Action of Carbon Monoxide on Potassium Cobalto Biscysteinate.—Measurements of the amount of carbon monoxide absorbed by potassium cobalto biscysteinate were made as described for the corresponding ferro complex. With the proportions of one mole of cobalt chloride, two of cysteine hydrochloride and six of potassium hydroxide the carbon monoxide absorbed amounted to about one mole in four hours after which there was no further absorption. The data for this are given in Table I, row 2, marked "equiv." But in these mixtures no complex at all analogous to the ferro biscysteinate dicarbonyl just described could be found. Two complexes of cobalt were, however, isolated, of which one contains only cysteine and the other only carbon and oxygen. The first, an oxidation product, is simply the green potassium cobalti triscysteinate, $K_3[Co(RS)_3]$ where R is the divalent radical ($—CH_2CHNH_2COO—$). The preparation of this complex from cobalt salt and cysteine has already been described.[4] The second complex could only be isolated as the silver and mercuric derivatives whose composition agrees reasonably with the formulas $Ag[Co(CO)_4]$ and $Hg[Co(CO)_4]_2$. In the flask described in the last section are placed 5 g. of cysteine hydrochloride and 15 cc. of 1 *M* cobalt chloride. After the air is completely displaced, 15 cc. of 6.3 *M* potassium hydroxide is added. Carbon monoxide is passed through while the mixture is shaken for four hours. At this point there always remains a small deposit of cobalt hydroxide.

To separate the green potassium cobalti triscysteinate and at the same time to show that its formation is not due to air oxidation occurring during its isolation, the stopcocks on the flask are closed and the whole flask set in the tank described previously[4] for the separation of complexes in the absence of air. After the air has been completely displaced from the tank by nitrogen and hydrogen, the flask is opened, 50 cc. of alcohol added to the contents and the mixture shaken. After an hour the mixture is filtered on a Buchner funnel, the solid dissolved in 40 to 50 cc. of water and reprecipitated with an equal volume of alcohol. After filtering, washing and drying in a vacuum, between 4 and 5 g. of product is obtained.

Anal. Calcd. for $K_3[Co(SR)_3]·3H_2O$: Co, 10.05; S, 16.35; N, 7.16; K, 19.93. Found: Co, 9.66; S, 16.02; N, 6.92; K, 20.41.

To show the presence of the second complex the following procedure was found best. To the mixture described above, after the absorption of carbon monoxide, there is added 100 cc. of acetone. After fifteen minutes the whole is filtered, and the filtrate quickly evaporated *in vacuo* to about 15 cc. To this is added a solution of a gram of mercuric chloride in 20 cc. of water and then after a few minutes 15 cc. of 6 *M* hydrochloric acid A yellow, more or less crystalline precipitate is obtained which is washed with dilute hydrochloric acid and then water. It can be recrystallized easily by dissolving in a small volume of acetone, filtering if necessary and then adding two volumes of water. The precipitate slowly crystallizes to yellow needles or rectangular yellow plates. It is dried *in vacuo* and protected from light; yield 0.5 g.

Anal. Calcd. for $Hg[Co(CO)_4]_2$: Hg, 37.00; Co, 21.78; C, 17.71; H, none. Found: Hg, 37.37, 37.52; Co, 21.16, 21.51; C, 17.38; H, 0.25.

This mercury salt is quite stable. It darkens when exposed to sunlight. It is very insoluble in water and non-oxidizing acids but dissolves readily in alcohol, ether, chloroform and acetone. It melts without apparent decomposition at 82°.

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(4) Schubert, THIS JOURNAL, 55, 3336 (1933).

To separate the silver salt, the procedure given above for the isolation of the mercury salt is followed as far as the evaporation of the acetone *in vacuo*. To the clear solution remaining after this evaporation there is added 5 cc. of concentrated ammonium hydroxide and as much of a solution of 2 g. of silver nitrate in 10 cc. of water plus 5 cc. of concentrated ammonium hydroxide as is necessary to cause complete precipitation. The precipitate, at first liquid, crystallizes rapidly. This is filtered off, washed with dilute ammonia, then with water, and dried in a desiccator over concentrated sulfuric acid at 1 mm. The product is light yellow and consists of needle-like crystals. It is not very stable, especially in air or when exposed to light, turning first gray, then black within an hour after its separation from solution. For this reason the analyses here given were run on samples which had been left in the desiccator only ten minutes. The water is probably residual moisture and the formula is not to be understood as implying the existence of a hydrate.

Anal. Calcd. for $Ag[Co(CO)_4]\cdot{}^1/_2H_2O$: Ag, 37.45; Co, 20.48; C, 16.66; H, 0.35. Found: Ag, 36.32; Co, 20.20; C, 16.42; H, 0.2.

Another preparation was apparently wetter.

Anal. Calcd. for $Ag[Co(CO)_4]\cdot 2H_2O$: Ag, 34.21; Co, 18.74; C, 15.42; H, 1.27. Found: Ag, 32.42; Co, 19.26; C, 14.89; H, 1.29.

This silver salt can be recrystallized from acetone just like the mercury salt. Its solubilities are similar to those of the mercury salt but it has no melting point, merely turning black when heated to about 90°. The yield of silver salt after recrystallization is about 400 mg.

IV. The Action of Carbon Monoxide on Potassium Cobalti Triscysteinate.—If larger quantities of potassium hydroxide are used in the experiment described in the last section, the absorption of carbon monoxide does not reach an end-point even after twenty-four hours and the amount of carbon monoxide absorbed in this period increases with the amount of potassium hydroxide used, as shown in Table I. In casting about for a possible explanation of this remarkable phenomenon it was found that potassium cobalti triscysteinate, one of the products of the reaction described in the last section, will itself absorb large quantities of carbon monoxide when in strongly alkaline solution and that this absorption is much slower than that discussed in the previous section, requiring twenty-four to forty-eight hours to approach completion. Table II shows that with a sufficient amount of alkali, one mole of this cobalti triscysteinate will absorb as much as five to six moles of carbon monoxide. One of the products of this reaction is potassium carbonate which was separated as barium carbonate while the other product is the same new complex described above, $Hg[Co(CO)_4]_2$, again separated as silver and mercury derivatives. In this reaction as in the preceding there again appears an oxidation product, the carbonate which could only have come from the carbon monoxide used.

The volume of carbon monoxide consumed was measured in a 500-cc. suction flask connected to a calibrated gas reservoir provided with a leveling tube and an outlet. In the bottom of the flask were placed small beakers containing the components of the mixtures described in Tables I and II. After sealing the connections with paraffin, carbon monoxide is passed into the suction flask, out the side arm through the gas reservoir, finally escaping through the outlet of the latter. When all the air has been displaced the whole apparatus is closed off by stopcocks and set on a shaking machine in a room kept at 30 ± 0.2°. When the system has come to temperature equilibrium the volume of gas in the reservoir is read, the beakers in the flask upset, mixing the components, and the shaking machine started.

To carry out the reaction described in this section, 5 g. of potassium cobalti triscysteinate, prepared as described elsewhere,[4] and 15 cc. water are placed in the flask described in the preceding section. After air has been removed by carbon monoxide

TABLE I

Millimoles of carbon monoxide absorbed by a mixture of 3.2 g. (20 mml.) of cysteine hydrochloride, 9.6 cc. of 1 *M* $CoCl_2$ solution and the number of cc. of 6.3 *M* KOH solution shown in column 1. The total solution volume is made up to about 40 cc. with water. Temperature 30°. The mixtures were shaken mechanically for the time indicated

Cc. of 6.3 KOH *M*	Millimoles of CO absorbed after the indicated number of hours 1	2	4	8	24	32
7.1	4.2	5.5	6.1	6.9	7.5	..
9.5 (equiv.)	7.8	9.0	9.4	9.5	9.7	9.7
10.0	8.3	11.0	12.1	12.2	12.4	12.3
15	3.6	6.9	10.8	15.8	25.9	27.8
20	3.5	7.0	12.0	19.1	34.9	36.3
25	4.7	9.0	13.2	22.4	38.5	42.0
30	3.8	7.6	12.3	21.7	39.6	43.2

TABLE II

Millimoles of carbon monoxide absorbed by a solution of 1 g. of the green potassium cobalti triscysteinate in 10 cc. of water with the addition of the number of cc. of 6.3 *M* KOH shown in column 1. One gram of this complex is 1.7 millimoles. The mixtures were shaken mechanically for the time indicated. Temperature, 30°

6.3 *M* KOH, cc.	Millimoles of CO absorbed after the indicated number of hours					
	1	2	4	8	24	32
0	0	0	0	0	0	0
1	0.2	0.6	1.7	3.3	5.1	5.3
2	.2	.5	1.6	3.8	7.1	7.6
3	.4	1.0	2.8	5.0	7.6	8.1
4	.4	1.3	3.6	6.9	8.9	9.0

20 cc. of 6.3 *M* potassium hydroxide, freed of carbonate by saturation with barium hydroxide, is added. The flask is then connected to a calibrated reservoir of carbon monoxide under slightly more than atmospheric pressure and shaken for about forty hours. Forty-five millimoles of carbon monoxide are absorbed. The very dark green color of the solution disappears in this time, only a light brown clear solution remaining. To separate the carbonate formed this solution is diluted with some water and about 25 cc. 1 *M* barium chloride added. The precipitate is filtered off, washed and dried and can be shown by a few simple tests and by barium analysis to be practically pure barium carbonate. Three and one-tenth grams is obtained.

The silver and mercury salts of the complex $H[Co(CO)_4]$ can be separated by extraction of the solution resulting from the carbon monoxide absorption with three 80-cc. portions of acetone and treatment of this acetone extract as already described. Two grams of the silver salt or 1.7 g. of the mercury salt is recovered after purification by recrystallization from acetone by addition of water. The properties and analyses of these two salts agree completely with those resulting from the reaction described in the preceding section.

V. The Formation of Cobalt Tetracarbonyl.—If either of the reaction mixtures produced by the absorption of carbon monoxide as described in the last two sections be diluted with two volumes of water and then acidified with hydrochloric acid, some gas is liberated and an extremely choking odor is produced strongly suggestive of impure acetylene. At the same time a yellow precipitate of plate-like crystals forms, extremely insoluble in water, dilute acids or alkalies. These are filtered off, washed with much water and set in a vacuum desiccator. They are very unstable in a dry state, so, like the silver salt described above, they must be analyzed after only a few minutes drying. Like the silver salt, they fortunately dry very quickly. The analysis and properties of these crystals correspond to those of cobalt tetracarbonyl.

Anal. Calcd. for $Co(CO)_4 \cdot {}^1/_2H_2O$: Co, 32.79; C, 26.67; H, 0.56. Found: Co, 32.70, 32.38; C, 25.88, 26.07; H, 0.48, 0.52.

The water in the formula is probably simply a residue of moisture and is calculated in this way merely for convenience. The yellow crystals are very unstable in air, usually turning black within an hour after their separation in a dry condition. They are volatile and have been sublimed *in vacuo*. No melting point could be obtained as the crystals sinter and decompose at 48 to 50° even under nitrogen. They dissolve readily in alcohol, ether, chloroform and benzene and such solutions show a slow evolution of gas and soon deposit a black amorphous precipitate. The crystals even after long washing with water persist in emitting traces of the choking acetylenic odor mentioned above and it cannot be decided at present whether this is the odor of the crystals themselves or of a product of their decomposition.

If the mixture described in section III be used to prepare the carbonyl a yield of 200 to 250 mg. is obtained, while from the mixture described in section IV 700 mg. results. Made from the mixture of section IV the carbonyl is never as pure as when made from the mixture of section III. This may be due to the fact that the reaction of section IV requires forty hours in the presence of strong alkali so that some decomposition or secondary reaction occurs, making it impossible to obtain as pure a product as from the mixture of section III where the conditions are milder.

VI. The Reaction of Cobalt Tetracarbonyl with Cysteine.—A half gram of freshly prepared cobalt tetracarbonyl is added to a solution of 2 g. of cysteine hydrochloride in 15 cc. water, 6 cc. 6.3 *M* potassium hydroxide and 15 cc. alcohol. The alcohol must be added as the carbonyl is too insoluble in water for any reaction to occur. With this mixture the carbonyl slowly goes into solution and at the same time a gas is evolved; 2.2 millimoles of gas are evolved, all of which is absorbed by ammoniacal cuprous chloride. The solution itself slowly deposits the characteristic green crystals of potassium cobalti triscysteinate even when the whole reaction is conducted under nitrogen in the tank used for the preparation of oxygen-sensitive compounds. Under these conditions 0.33 g. of the green complex have been obtained after recrystallization from water by addition of alcohol. Finally there was separated by the method described in section III, between 0.4 and 0.5 g. of the compound $Hg[Co(CO)_4]_2$.

VII. Discussion of Results.—The mixture discussed in section III has been shown[4] to give rise to the following reaction in the absence of air: $CoCl_2 + 2HSRH \cdot HCl + 6KOH \longrightarrow K_2[Co(SR)_2] + 4KCl + 6H_2O$ where R has the meaning defined in section III. When carbon monoxide is passed through this solution, it is quite possible that the first reaction is the same as that described in section II for the corresponding iron complex where potassium ferro biscysteinate dicarbonyl is the product. But whereas the iron complex is stable in this ferrous state the cobalt in the analogous hypothetical complex, having a greater tendency to assume the trivalent condition, does so at the expense of reducing some other reactant. The equation for the total reaction can be written

$$9K_2[Co(SR)_2] + 8CO + 2H_2O \longrightarrow 6K_3[Co(SR)_3] + 2H[Co(CO)_4] + Co(OH)_2 \qquad (1)$$

The formation of carbonate in the reaction of section IV means that this is also an oxidation–reduction reaction. It can be represented thus

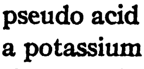
$$K_3[Co(SR)_3] + 6CO + 7KOH \longrightarrow H[Co(CO)_4] + 2K_2CO_3 + 3K_2(RS) + 3H_2O \qquad (2)$$

The assumptions and reasoning made use of for arriving at equations (1) and (2) cannot be given here for lack of space but a study of the data given in sections III and IV will show that all the products and only those demanded by these equations were actually found. Furthermore, the quantities of reactants and products will be found to be in fair agreement with these equations particularly considering that wherever possible products were purified by recrystallization.

No adequate formulation of the reaction described in section V can be given as it has been impossible so far to account for the hydrogen which it has been assumed occurs in the cobalt tetracarbonyl hydride. When this compound is, in part at least, converted to cobalt tetracarbonyl either free hydrogen or some reduction product, possibly of carbon monoxide, would be expected to result but none such could be found.

Finally, the following equation agrees very well both qualitatively and quantitatively with the products found for the reaction of section VI.

$$4Co(CO)_4 + 3H_2RS + 3KOH \longrightarrow 3H[Co(CO)_4] + K[Co(RS)_3] + 4CO + 3H_2O \quad (3)$$

Although equations (1), (2) and (3) seem to summarize correctly the experimental findings, there remains the ambiguity attaching to the unformulated constitution of $H[Co(CO)_4]$. An assumption that has been found useful as a working hypothesis in dealing with these unusual reactions is that in the formation of the new complex the carbon monoxide has been reduced to a divalent negative radical $(C_2O_2)^{=}$. The only two plausible structure which can be suggested for this radical are (—OC≡CO—) and  $(-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-)$. The first has already been suggested by Reihlen[5] in his studies on iron carbonyls and their derivatives. The second has been suggested by Joannis,[6] who isolated the compound $K_2C_2O_2$ by the action of carbon monoxide on a liquid ammonia solution of potassium.

On this view the new complex would be a cobalti complex of a divalent pseudo acid radical, $H[Co(C_2O_2)_2]$ which in alkaline solution might exist as a potassium salt. This suggests the interpretation of the oxidation-reduction reactions (1) and (2). In fact if the essential part of (2) is written alone, we have: $3CO + 4(OH)^- \longrightarrow (C_2O_2)^{=} + CO_3^{=} + 2H_2O$. It thus resembles a Cannizzaro reaction on a free carbonyl group occurring appropriately in strong alkali.

Cobalt carbonyl has usually been regarded like most of the metal carbonyls as being a pure coördination compound, that is, as being composed of zero valent cobalt and coördinatively bound carbon monoxide. Reaction (3) which can be carried out completely in the absence of air and in which no stronger oxidant than water is present gives as products one complex, the cobalti triscysteinate, in which the cobalt is certainly trivalent and another in which it is probably trivalent. With this reaction in mind it seems difficult to regard the cobalt in the carbonyl as zero valent. The

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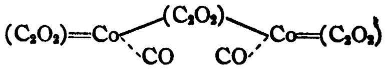
(5) Reihlen and co-workers, *Ann.*, **465**, 72 (1928); **472**, 268 (1929).

(6) M. A. Joannis, *Compt. rend.*, **116**, 1518 (1893); **158**, 874 (1914).

following structure involving trivalent cobalt would be much more in agreement with the experiments described here.



$$(C_2O_2){=}\mathrm{Co}\underset{\mathrm{CO}\qquad\mathrm{CO}}{\overset{(C_2O_2)}{\diagup\qquad\diagdown}}\mathrm{Co}{=}(C_2O_2)$$

This formula in addition to accounting for reaction (3) would explain why cobalt tetracarbonyl is dimolecular and why it loses two moles of carbon monoxide rather easily to form cobalt tricarbonyl.

Hieber[7] describes a reaction of acid with tricarbonyl-*o*-phenanthroline cobalt among the products of which is cobalt tetracarbonyl and a carbonyl compound with hydrogen attached directly to the cobalt, $[Co(CO)_4H]$, as well as a volatile unstable cobalt compound with an evil odor. The cobalt carbonyl hydrogen compound, for whose existence Hieber defers giving any evidence, might be one assumed here from which the mercury and silver compounds are derived.

Hieber[8] has also described a reaction of $Fe(CO)_5$ in strong alkali which bears some resemblance to the reaction of section IV. He formulates it as: $Fe(CO)_5 + 2(OH)^- \longrightarrow [Fe(CO)_4H_2] + CO_3^{=}$. The hydrogen in the iron carbonyl hydride is regarded as being attached directly to the iron by a peculiar kind of bond.

Further study of these compounds would no doubt add to our knowledge of valence.

Mr. G. Bitterlich of this Laboratory carried out all the analytical work described here.

Summary

The complex ferro biscysteinate dicarbonyl has been crystallized as a free acid and as its sodium salt. The action of carbon monoxide on potassium cobalto biscysteinate has been shown to involve oxidation and reduction, the products being the green potassium cobalti triscysteinate and a new complex, isolated as the silver and mercury compound, apparently derived from $H[Co(CO)_4]$. The action of carbon monoxide on the green potassium cobalti triscysteinate in strong alkali also involves oxidation and reduction, the products being carbonate and the new complex $H[Co(CO)_4]$. The complex $H[Co(CO)_4]$, on treatment with acid, gives cobalt tetracarbonyl. Cobalt tetracarbonyl on treatment with cysteine and alkali gives potassium cobalti triscysteinate and $H[Co(CO)_4]$.

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[7] W. Hieber, F. Muhlbauer and E. A. Ehmann, *Ber.*, **65**, 1090 (1932).

[8] W. Hieber and F. Leutert, *Z. anorg. allgem. Chem.*, **204**, 155 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

The Action of Formaldehyde on Amines and Amino Acids[1]

BY H. T. CLARKE, H. B. GILLESPIE AND S. Z. WEISSHAUS

The convenient method due to Sommelet and Ferrand[2] for the preparation of trimethylamine from ammonium formate, formaldehyde and formic acid, though its usefulness has recently been demonstrated[3] in the case of anabasine, appears not to have attained general recognition as a means for the methylation of amines.

This process furnishes excellent yields of tertiary bases from simple primary and secondary aliphatic amines, including piperidine. Its ready applicability is illustrated by the complete methylation of tetramethylenediamine, the hydrochloride of which is extensively decomposed by heating at 125° with aqueous formaldehyde,[4] and yields the tetramethyl derivative only when heated to 200° with dry paraformaldehyde.[5]

The reaction appears to be specific for formaldehyde, in contrast to its homologs, which apparently require higher temperatures[6] for corresponding changes to take place. Thus, a mixture of acetaldehyde, formic acid and ammonium formate yielded no carbon dioxide on heating on the steam-bath, and from the resulting bases only 2-methyl-5-ethylpyridine could be isolated. The reaction also fails with compounds in which strongly polar groups are attached to nitrogen, such as amides, urea, guanidine and hydroxylamine; these appear to yield hydroxymethyl derivatives only. Moreover, it cannot be applied successfully to the methylation of aniline, which on warming with formaldehyde in formic acid solution is converted into condensation products of high molecular weight.[7] On the other hand, 2,4,6-tribromoaniline, in which the sensitive positions in the benzene nucleus are occupied, is smoothly converted into its dimethyl derivative.

In the production of tertiary amines in this way, one molecular proportion (or slightly more) of formaldehyde has been found sufficient for each methyl group introduced. It is therefore mainly the formic acid which supplies the hydrogen involved in the reduction

$$R_2NH + CH_2O + HCO_2H = R_2NCH_3 + CO_2 + H_2O \qquad (1)$$

This is confirmed by the behavior of hexamethylenetetramine, in which only one-half of the amount of formaldehyde necessary for the formation of trimethylamine is potentially present. In the final mixture of products 70–80% of the methylene carbon reappears as methyl group, mainly in the form of trimethylamine, as has been demonstrated by Sommelet and Ferrand.[8] The deficiency of carbon must be due to the participation in the reduction of some of the formaldehyde liberated by hydrolysis, and not to the escape of formaldehyde nor to the production of methyl alcohol, for these have been shown not to occur to a significant extent. Moreover, less than 70% of the calculated amount of carbon dioxide is produced; this appears to be general in methylation reactions involving formaldehyde and formic acid, and furnishes a contrast to the theoretical yield[9] obtainable in the reaction between formic acid and triphenylcarbinol.[10] The hydrogen-donating function of formaldehyde, which constitutes an important feature in the Plöchl process[11] for methylation with formaldehyde alone, finds a counterpart in the behavior of the carbinol group in ethyl-α-pyrrolidylcarbinol and similar compounds;[12] this is converted into carbonyl during methylation by formaldehyde alone, but remains unaffected when the reaction is carried out in the presence of formic acid.

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(1) This work was aided by a grant from The Chemical Foundation.

(2) Sommelet and Ferrand, *Bull. soc. chim.*, [4] **35**, 446 (1924).

(3) Orechoff and Norkina, *Ber.*, **65**, 724 (1932).

(4) Clarke, *J. Chem. Soc.*, **103**, 1700 (1913).

(5) Keil, *Z. physiol. Chem.*, **196**, 81 (1931).

(6) Wallach, *Ann.*, **343**, 54 (1905).

(7) *Cf.* Wagner, THIS JOURNAL, **55**, 724 (1933).

Werner's[13] explanation of the production of trimethylamine by the action of formaldehyde upon ammonium chloride involves the scission of tetramethyldiaminomethane into trimethylamine and methylenemethylamine, which in turn accepts hydrogen from formaldehyde

$$\mathrm{Me_2NCH_2NMe_2{\cdot}2HCl = Me_3NHCl + CH_2{=}NMe{\cdot}HCl}$$
$$\mathrm{CH_2{=}NMe{\cdot}HCl + CH_2O + H_2O = CH_3NHMe{\cdot}HCl + HCOOH}$$

In the methylation of simple amines by formaldehyde in formic acid this type of disruption appears not to occur, for secondary amines other than dimethylamine are converted, in excellent yields, into their N-methyl derivatives. Of those studied, the least favorable results were given by dibenzylamine, from which 75% of the amount of methyldibenzylamine anticipated according to Reaction 1 was secured. Tetrabenzyldiaminomethane reacts with formic acid to yield equivalent amounts of methyldibenzylamine and dibenzylamine

$$\mathrm{(PhCH_2)_2NCH_2N(CH_2Ph)_2 + HCOOH = (PhCH_2)_2NCH_3 + (PhCH_2)_2NH + CO_2} \quad (2)$$

Were the preponderating reaction of the type analogous to that described by Werner, the primary products would have been methyldibenzylamine and benzalbenzylamine

$$\mathrm{(PhCH_2)_2NCH_2N(CH_2Ph)_2 = (PhCH_2)_2NCH_3 + PhCH{=}NCH_2Ph} \quad (3)$$

and the latter would, as we have found by experiment, immediately be hydrolyzed by the formic acid.[14] Benzaldehyde is not formed to any

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(8) Sommelet and Ferrand, *Bull. soc. chim.*, [4] 25, 457 (1919); 35, 446 (1924).

(9) A 99.1% yield of carbon dioxide was secured in this reaction when carried out under the conditions adopted for the present experiments.

(10) Kauffmann and Pannwitz, *Ber.*, 45, 766 (1912); Kovache, *Ann. chim.*, [9] 10, 184 (1918).

(11) Plöchl, *Ber.*, 21, 2117 (1888).

(12) Hess, *ibid.*, 46, 4104 (1913); Hess, Merck and Uibrig, *ibid.*, 48, 1886 (1915).

(13) Werner, *J. Chem. Soc.*, 111, 844 (1917).

(14) Benzalmethylamine is also hydrolyzed on warming with formic acid, no evolution of carbon dioxide nor reduction to methylbenzylamine taking place.

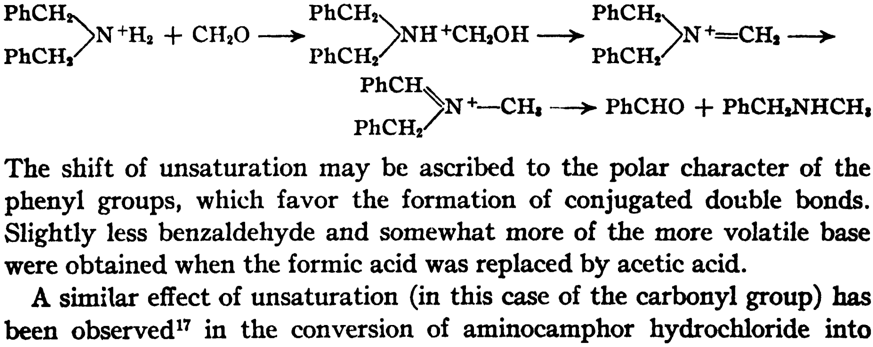
appreciable extent. Methylenedipiperidine also furnishes a clear-cut example of the type of Reaction 2.

It therefore appears reasonable to suppose that in the above case, as in that of simple amines, the main methylation reaction consists in the formation and subsequent reduction of a methylol derivative by the formic acid. As has been suggested by Emde,[15] this possibly involves the thermal decomposition of the formic ester

$$R_2NCH_2NR_2 \longrightarrow R_2NH + R_2NCH_2OH \longrightarrow R_2NCH_2OCHO \longrightarrow R_2NCH_3 + CO_2$$

The analogous formation of saturated hydrocarbons by pyrolysis of formic esters appears to be a general reaction.[16] The ease with which it can take place probably depends upon the degree of polarity of the groups attached to the carbinol carbon atom; thus, triphenylcarbinol is reduced by formic acid at temperatures below 100°.

Among the products of the reaction of dibenzylamine with excess of formaldehyde in formic acid there occurs 6–12% of a more volatile base, probably dimethylbenzylamine, and a corresponding amount of benzaldehyde. Since, as above stated, benzaldehyde is barely detectable among the products of the action of formic acid upon tetrabenzyldiaminomethane, its formation cannot be explained along the lines of Reaction 3, but rather as a result of a rearrangement of a methylene derivative of an ammonium ion



$$\left.\begin{matrix}PhCH_2\\PhCH_2\end{matrix}\right>N^+H_2 + CH_2O \longrightarrow \left.\begin{matrix}PhCH_2\\PhCH_2\end{matrix}\right>NH^+CH_2OH \longrightarrow \left.\begin{matrix}PhCH_2\\PhCH_2\end{matrix}\right>N^+{=}CH_2 \longrightarrow$$

$$\left.\begin{matrix}PhCH\\PhCH_2\end{matrix}\right>N^+{-}CH_3 \longrightarrow PhCHO + PhCH_2NHCH_3$$

The shift of unsaturation may be ascribed to the polar character of the phenyl groups, which favor the formation of conjugated double bonds. Slightly less benzaldehyde and somewhat more of the more volatile base were obtained when the formic acid was replaced by acetic acid.

A similar effect of unsaturation (in this case of the carbonyl group) has been observed[17] in the conversion of aminocamphor hydrochloride into camphorquinone by heating with formaldehyde.

The behavior of aliphatic amino acids toward formaldehyde similarly displays the effect of the unsaturation inherent in the carboxyl group. Zeleny and Gortner[18] have recently shown that when alanine, glutamic acid, tyrosine and cystine are boiled with an excess of formaldehyde in 20% hydrochloric acid, as much as 40% of the nitrogen is eliminated as methylamine. We find analogous decompositions to take place on warming amino acids with formaldehyde in formic and acetic acids. Glycine under

(15) Emde, *Apoth. Zeit.*, **44**, 1125 (1929); Emde and Hornemann, *Helv. Chim. Acta*, **14**, 892 (1931).

(16) Bayer & Co., German Patent 296,741 (*Chem. Zentr.*, [1] 611 (1917).

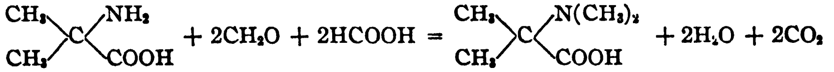
(17) Rupe, Buxtor and Flatt, *Helv. Chim. Acta*, **13**, 1026 (1930).

(18) Zeleny and Gortner, *J. Biol. Chem.*, **90**, 427 (1931).

these conditions yields 60–70% of dimethylglycine, but at the same time considerable amounts of more complex, non-crystallizable products, as well as 6% of volatile base (mostly trimethylamine) are formed in the reaction. β-Aminopropionic acid behaves in much the same way, though the yield of the dimethyl derivative is distinctly lower.

With alanine, on the other hand, none of the dimethyl derivative could be secured; a complex mixture was formed, and 36% of the nitrogen was converted into methylamines. Similar results were obtained with leucine, α-aminocaprylic acid and glutamic acid, in all of which an even greater proportion of the nitrogen was split off. When the formic acid was replaced by acetic acid, volatile bases were produced, but definitely less carbon dioxide was liberated.

The view that the deamination is associated with migration of unsaturated linkages is supported by the observation that α-aminoisobutyric acid, in which such migration is clearly impossible without decarboxylation, is converted into its dimethyl derivative in 80% yield



$$(CH_3)_2C(NH_2)COOH + 2CH_2O + 2HCOOH = (CH_3)_2C(N(CH_3)_2)COOH + 2H_2O + 2CO_2$$

In this reaction over 88% of the theoretical amount of carbon dioxide was recovered, and only 5% of the nitrogen was detached.

α-Aminophenylacetic acid on treatment with formaldehyde and formic acid gave up over 50% of its nitrogen, together with an appreciable quantity of benzaldehyde. Inasmuch as benzylamine yields little or no benzaldehyde under these conditions, the disruptive effect must here be ascribed to the combined influence of the phenyl and carboxyl groups. With acetic acid in place of formic acid, benzaldehyde was likewise found, and a notable proportion of the nitrogen was released as volatile base; the yield of carbon dioxide was much lower. It is difficult to avoid speculation as to an analogy between this reaction and the formation of acetylamino ketones from amino acids and acetic anhydride in presence of pyridine.[19] The possibility that at least a part of the carbon dioxide was derived from the carboxyl group is supported by the observation that α-aminophenylacetic acid yields benzylamine as the sole volatile base on heating in acetic acid solution with heptaldehyde. The formation of benzaldehyde is undoubtedly due to a secondary reaction which invites comparison with the "oxidative deamination" reaction between α-amino acids and furfural[20] or methylglyoxal.[21]

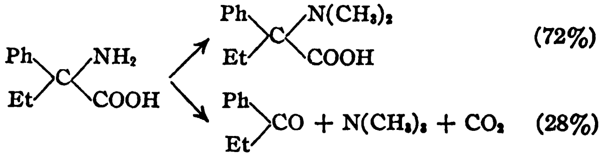
α-Phenyl-α-aminobutyric acid with formaldehyde in formic acid gave a 72% yield of its dimethyl derivative, 10–16% of the nitrogen appearing in volatile form. The yield of carbon dioxide closely approximated the

(19) Dakin and West, *J. Biol. Chem.*, **78**, 91, 745 (1928).

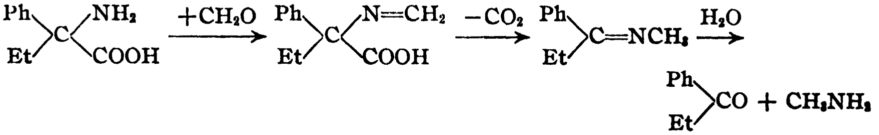
(20) Akabori, *Ber.*, **66**, 143 (1933).

(21) Kisch, *Biochem. Z.*, **257**, 334 (1933).

theoretical value, an effect which may reasonably be ascribed to the promotion of decarboxylation under the influence of the phenyl group. This hypothesis is supported by the isolation of 28% of propiophenone

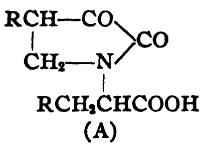


The side reaction, resulting in the formation of the ketone, probably takes the course



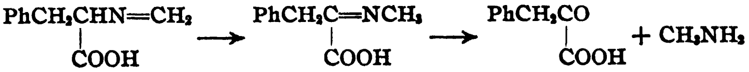
With amino acids of higher molecular weight, treatment with formaldehyde in either formic or acetic acid generally resulted in the formation of neutral nitrogenous products which were soluble in ether. This was also observed in the reactions with heptaldehyde. The physical character of these products, however, stood in the way of their detailed study.

dl-Phenylalanine with formaldehyde, in either formic acid or acetic acid solution, yielded a crystalline acid having the composition $C_{19}H_{17}O_4N$. An optically active variety of this acid was prepared from *l*-phenylalanine, and an optically active dimethoxy analog was obtained from *l*-*p*-methoxyphenylalanine.[22] These compounds are derivatives of pyrrolidinedione; the evidence for the structure (A) is presented in the experimental part of this report. Like the triphenylpyrrolidinedione prepared by Borsche[23] from phenylpyruvic acid, benzaldehyde and aniline, they react exclusively in the enolic form, yielding green colors[24] with ferric chloride in alcohol and failing to yield hydrazones and similar ketonic derivatives under the usual conditions.



(A)

The formation of pyrrolidinedione from phenylalanine apparently involves the rearrangement of a methylene derivative, followed by hydrolysis to phenylpyruvic acid and methylamine



$$\underset{COOH}{\underset{|}{PhCH_2CHN{=}CH_2}} \longrightarrow \underset{COOH}{\underset{|}{PhCH_2C{=}NCH_3}} \longrightarrow \underset{COOH}{\underset{|}{PhCH_2CO}} + CH_3NH_2$$

The phenylpyruvic acid then condenses with formaldehyde and a second molecule of phenylalanine, in analogy with the syntheses of triphenyl-

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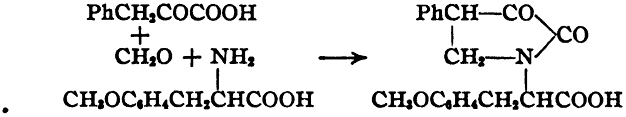
(22) Behr and Clarke, THIS JOURNAL, 54, 1630 (1932).

(23) Borsche, *Ber.*, 41, 3884 (1908); 42, 4072 (1909).

(24) We have found that triphenylpyrrolidinedione in alcoholic solution develops with ferric chloride a green color resembling that obtained with phenylpyruvic acid.

pyrrolidinedione and of β-amino ketones.[25] The same product is equally readily formed from phenylalanine and formaldehyde in acetic acid solution; in this case the nitrogen eliminated in the reaction reappears almost entirely as methylamine. A similar yield was obtained on replacing half of the phenylalanine by a semi-equivalent amount of phenylpyruvic acid, when much less volatile base was formed. Even stronger evidence for the correctness of the above view is furnished by the formation, in excellent yield, of the corresponding monomethoxy derivative from phenylpyruvic acid, formaldehyde and *p*-methoxyphenylalanine



Since, as above stated, the volatile bases formed by the action of formaldehyde upon alanine in acetic acid likewise consist principally of monomethylamine, it seems logical to attribute the partial deamination of other amino acids by formaldehyde to a similar series of reactions.

Experimental

Methylation of Simple Amines.—One mole of the primary amine was added, with cooling, to 5 moles of formic acid (90%); 2.2 moles of formaldehyde (35% solution) was added. For secondary amines, half these quantities of acid and aldehyde were taken, though in either case excess does no harm. The mixture was heated on the steam-bath under reflux for two to four hours after evolution of gas had ceased (eight to twelve hours in all). Slightly more than one mole of hydrochloric acid was then added, and the formic acid and any excess formaldehyde were evaporated on the steam-bath. The colorless residue was dissolved in water, rendered alkaline with excess of 25% sodium hydroxide solution, and the base distilled out. The distillate was saturated with potassium hydroxide, the oil was separated, dried by heating with solid potassium hydroxide and distilled over sodium. In this way the following bases were obtained in yields of over 80%; dimethyl-*n*-butylamine, b. p. 94°; dimethylbenzylamine, b. p. 176–180°; methylpiperidine, b. p. 106°.

1,4-Tetramethyldiaminobutane.—To a solution of 4.6 g. of sodium bicarbonate in 18 cc. of 95% formic acid were added 4.0 g. of 1,4-diaminobutane hydrochloride and 10 cc. of formalin. The mixture was boiled under reflux for thirty-five hours, diluted with an equal volume of water containing 6 cc. of 10 *N* hydrochloric acid, and evaporated to dryness. The residue was redissolved in water, and the base isolated as above described, when 3.3 g. (92% of the theoretical amount) of the pure 1,4-tetramethyldiaminobutane, b. p. 167°, was secured. The picrate melted at 198–199°.

Aromatic Amines.—Treatment of aniline in formic acid with formalin led to the formation of a viscous oil, practically none of which was volatile with steam. With 2,4,6-tribromoaniline, on the other hand, methylation proceeded smoothly: a solution of 10 g. of the amine in 150 cc. of 90% formic acid and 10 cc. of formalin was boiled under reflux for two hours. After the addition of 3–5 cc. of concentrated hydrochloric acid and removal of most of the formic acid under reduced pressure, the residue was made alkaline and distilled with steam. The heavy oil which passed over was collected and redistilled; it boiled at 295–300° (uncorr.). The yield was 9.3 g. (77% of the calculated amount). As no rise in temperature was observed on adding acetic anhydride (with which the oil is only sparingly miscible) the product consists of a tertiary amine. It was definitely identified in the form of the perbromide[26] which melted at 124–125° with evolution of gas.

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[25] Mannich, *Arch. Pharm.*, **255**, 261 (1917); *Ber.*, **53**, 1874 (1920); Bodendorf and Koralewski, *Arch. Pharm.*, **271**, 101 (1933).

Dibenzylamine and Formaldehyde.—A mixture of 19.7 g. of dibenzylamine (0.1 mole), 25 cc. of 90% formic acid and 12 cc. of formalin was heated on the steam-bath for eighteen hours; it was then treated with 120 cc. of normal sulfuric acid and distilled in a current of steam. Benzaldehyde was extracted with chloroform from the distillate and yielded 1.87 g. of the phenylhydrazone (m. p. 155–157°). According to control experiments carried out in the presence of comparable amounts of formic acid and formaldehyde, this corresponds to about 12 millimoles of benzaldehyde. The residual acid solution was rendered alkaline and distilled at constant volume in a current of steam: seven successive 50–55 cc. fractions, collected and titrated separately, showed the presence of 11.8, 5.0, 3.1, 2.6, 2.2, 2.2, 2.2 milliequivalents of base, respectively. Neglecting the retention of methyldibenzylamine in the first four fractions due to the presence of a more volatile base, the amount of the latter (undoubtedly dimethylbenzylamine) may be inferred to have been about 13 m. eq. The less volatile methyldibenzylamine which had distilled, therefore, amounted to 16 m. eq.; the undistilled balance was isolated from the residue in a yield of 13.0 g. (61 m. eq.); after the removal of 2.5 m. eq. of base which reacted with acetic anhydride, it boiled at 146–147° (7 mm.) and contained 6.62% of N (calcd., 6.60).

In a parallel experiment with 7.1 g. (36 m. eq.) of dibenzylamine and 4.5 cc. of formalin in 11 cc. of acetic acid, 0.370 g. of benzaldehydephenylhydrazone (1.84 millimoles) was secured, while the presence of 9.4 m. eq. of more volatile bases was indicated by the distillation procedure.

Action of Formic Acid on Tetrabenzyldiaminomethane and on Methylenedipiperidine.—A solution of 3.344 g. of tetrabenzyldiaminomethane[27] (m. p. 99–101°) in 30 cc. of 90% formic acid was heated on the steam-bath under reflux for eight hours. After the addition of 3 cc. of concentrated hydrochloric acid, the mixture was distilled in a current of steam; the distillate contained only a trace of benzaldehyde, detected by a very faint odor. The residue was diluted to 500 cc. and an aliquot portion treated with alkali and benzenesulfochloride, then acidified and filtered free of benzenesulfonyl compounds. The filtrate contained 45.6% of the nitrogen in the form of tertiary amines.

An analogous experiment with 13.4 g. of methylenedipiperidine in 40 cc. of 90% formic acid gave 52.1% of the nitrogen as crystalline benzenesulfonylpiperidine and 45.3% as methylpiperidine.

Action of Formic Acid on Benzalbenzylamine.—A solution of 10 cc. of benzaldehyde in 5 cc. of alcohol was added to 10 cc. of benzylamine in 50 cc. of water. The heavy oil which separated, with evolution of heat, was collected and distilled[28] (b. p. 143–144° (5 mm.)).

Anal. Calcd. for $C_{14}H_{13}N$: N, 7.18. Found: N, 6.98.

On adding 2.05 g. of this product to 10 cc. of 90% formic acid the temperature rose slightly, and the odor of benzaldehyde at once appeared. The mixture was heated on the steam-bath for forty-four hours without appreciable evolution of carbon dioxide; on distilling in a current of steam, benzaldehyde passed over, and benzylamine was recovered from the residual solution.

Action of Formic Acid on Hexamethylenetetramine.—A solution of 0.560 g. (4 millimoles) of hexamethylenetetramine in 25 cc. of 90% formic acid (freed of dissolved

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(26) Fries, *Ann.*, 346, 200 (1906).

(27) Von Braun and Röver, *Ber.*, 36, 1196 (1903).

(28) Mason and Winder, *J. Chem. Soc.*, 65, 91 (1894), report b. p. 200–202° (10–20 mm.).

carbon dioxide) was boiled under reflux in a slow current of nitrogen for ten hours. The carbon dioxide evolved during the reaction was collected in barium hydroxide and estimated by titrating the precipitated barium carbonate with standard acid; it amounted to 33.6 m. eq. or 68.9% of the quantity theoretically obtainable. The residual solution was treated with excess of hydrochloric acid and freed of formic acid by evaporation; the residue was treated with alkali and the volatile bases again distilled out and converted into their hydrochlorides. These were dried as completely as possible and repeatedly extracted with boiling chloroform, which dissolved the salts of dimethylamine and trimethylamine. The amounts of these were determined on aliquot portions by estimating the volatile bases before and after treatment in dilute alkaline solution with benzenesulfochloride. The chloroform-insoluble residue, containing the hydrochlorides of ammonia and methylamine, was treated in dilute alkaline solution with mercuric oxide according to the method of Weber and Wilson[29] for the separation of these two bases. The values for the nitrogen distribution: NH_3, 9.28; CH_3NH_2, 0.85; $(CH_3)_2NH$, 0.70; $(CH_3)_3N$, 5.09—total, 15.92 m. eq.—correspond to 99.5% of the calculated amount of nitrogen but to only 73% of the carbon in the hexamethylenetetramine taken.

That the deficiency of carbon is not due to the escape of formaldehyde nor to the formation of methyl alcohol (or formate) was proved by boiling a solution of 10 g. of hexamethylenetetramine in 80 cc. of formic acid for six hours, collecting the evolved carbon dioxide in cold aqueous sodium hydroxide, and then distilling 6.5 cc. of the residual mixture. The distillate was rendered alkaline, united with the absorption liquid, and again distilled. Oxidation of an aliquot portion of the resulting distillate by standard dichromate indicated the presence of less than 10 mg. of methyl alcohol; *i. e.*, less than 0.1% of the amount corresponding to the carbon content of the hexamethylenetetramine. Formaldehyde was not detectable by ammoniacal silver nitrate.

Action of Acetaldehyde on Ammonia in Formic Acid.—To a cold mixture of 167 cc. of 90% formic acid and 11 cc. of 28% aqueous ammonia (0.2 mole) was added 33 cc. of acetaldehyde (0.6 mole). The whole was gently warmed on the steam-bath under reflux. Carbon dioxide was not evolved. After forty-two hours of heating the basic products were isolated; these consisted of ammonia and 2.5 cc. of a weakly basic oil which yielded 3.0 g. of 2-methyl-5-ethylpyridine picrate of m. p. 162–164°.

Action of Formaldehyde and Heptaldehyde on Amino Acids.—Two series of preliminary experiments were run with amino acids (2–5 millimoles), using rather more than twice the equivalent quantities of formaldehyde and carbon dioxide-free formic acid and acetic acid, respectively, as reaction media. Varying the proportions of the latter within wide limits had no apparent effect on the relative amounts of volatile base and carbon dioxide produced. Boiling was continued until the reaction had come to an end (three to eight hours).

The results are presented in Tables I and II. To these may be added a few points of detail. In the reaction of leucine with formaldehyde and formic acid, a neutral ether-soluble oil was formed; a similar product was obtained from α-aminocaprylic acid, and was found to contain 44.6% of the nitrogen. α-Aminophenylacetic acid also yielded an ether-soluble fraction containing 6.5% of the nitrogen; at the same time an appreciable quantity of benzaldehyde was formed. This occurred also in acetic acid; analysis of the volatile bases (25.1% of the nitrogen) produced in a parallel experiment in acetic acid, showed the nitrogen distribution to be 18.6% ammonia, 51.2% primary amines, and 30.2% di- and trimethylamines.

A few similar experiments were carried out with heptaldehyde in formic acid and acetic acid. To the information reported in Table III should be added the following: in Expt. 1 practically all of the non-volatile nitrogen in the aqueous solution was found to be in the primary amino form. In Expt. 2 the neutral ethereal extract was separated

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[29] Weber and Wilson, *J. Biol. Chem.*, **35**, 385 (1918).

TABLE I

AMINO ACIDS WITH FORMALDEHYDE IN FORMIC ACID

Amino acid	CO_2, moles per amino group	Volatile bases, % of total N
Glycine	1.55	5.7
Alanine	1.10	36.4
β-Aminopropionic	1.75	8.3
α-Aminoisobutyric	1.77	5.3
Leucine	..	25.5
Glutamic	1.43	51.4
α-Aminocaprylic	..	32.3
α-Aminophenyl-acetic	1.34	53.9
Phenylalanine	1.30	51.8
α-Amino-α-phenyl-butyric	1.99	10.6
Cystine	1.67	31.4

TABLE II

AMINO ACIDS WITH FORMALDEHYDE IN ACETIC ACID

Amino acid	CO_2, moles per amino group	Volatile bases, % of total N
Glycine	0.49	15.1
Alanine	.41	13.2
β-Aminopropionic	.52	23.6
α-Aminoisobutyric	.81	29.8
α-Aminophenyl-acetic	.80	43.0
Phenylalanine	.60	26.0
Cystine	1.29	23.1

into two fractions, (a) soluble in petroleum ether, 5.834 g. containing 7.6 m. eq. of nitrogen (15.2%), and (b) insoluble in petroleum ether but soluble in benzene, 1.526 g. containing 4.75 m. eq. of nitrogen (9.5%). In Expt. 3 one-half of the nitrogen in the ether extract was in the primary amino form, while all of that in the water solution was amino nitrogen. In Expt. 4 the volatile base consisted entirely of benzylamine, b. p. 180–190°, identified as dibenzyloxamide, m. p. 216°. The oily ether-soluble fraction, weighing 7.1 g., was distilled under reduced pressure, when about half of it passed over at 180–190° (10 mm.) before decomposition set in. The distillate partially crystallized on cooling, yielding colorless leaflets, m. p. 57°, very soluble in alcohol and ether, but sparingly in petroleum ether, and containing: C, 72.82; H, 7.55; N, 8.3. It is doubtful if the product was homogeneous; the amount available was too small for further study.

TABLE III

ACTION OF HEPTALDEHYDE ON AMINO ACIDS

Expt.	Amino acid	Acid	Time and temp. of heating Hours	t, °C.	Volatile N, %	Ether-soluble N, %	Water-soluble N, %
1	Alanine	HCOOH	16	90	1.3	2.65	95
2	Alanine	AcOH	40	115	7.4	24.7	56
3	α-Aminophenylacetic	HCOOH	16	90	13.8	46.3	36
4	α-Aminophenylacetic	AcOH	21	115	13.6	61.4	..

In several instances the reaction with formaldehyde was investigated more closely on a larger scale; the more significant of such experiments are reported in detail.

Dimethylglycine Hydrochloride.—A mixture of 22.5 g. (0.3 mole) of glycine, 75 cc. of 90% formic acid and 60 cc. of formalin was gently boiled under reflux for seventeen hours; 30 cc. of concentrated hydrochloric acid was added, and the solution was evaporated to a sirup under reduced pressure. The crystals which separated on cooling were collected, washed with acetic acid, dried and recrystallized from water. The mother liquor yielded 27–28 g. (64–67% of the calculated quantity) of dimethylglycine hydrochloride as needles of m. p. 189–190° (uncorr.), readily soluble in water and alcohol, sparingly soluble in cold but readily in warm acetic acid, insoluble in chloroform and acetone.

Anal. Calcd. for $C_4H_{10}O_2NCl$: C, 34.5; H, 7.17; N, 10.03; Cl, 25.4. Found: C, 34.70, 34.56; H, 7.11, 6.81; N, 10.02; Cl, 25.36.

The free dimethylglycine was prepared as an extremely hygroscopic solid by treating a cold aqueous solution with an exactly equivalent quantity[30] of freshly-precipitated silver oxide, filtering and evaporating to dryness.

The ethyl ester was identical with that described by Willstätter.[31] It boiled at 149°.

Anal. Calcd. for $C_6H_{13}O_2N$: C, 54.9; H, 9.93; N, 10.68. Found: C, 54.7, 54.9; H, 9.68, 9.63; N, 10.47.

On hydrolysis with dilute hydrochloric acid, the original hydrochloride, m. p. 189–190°, was regenerated.

The united mother liquors from an experiment which had given a 67% yield of dimethylglycine hydrochloride contained 60.5 m. eq. of nitrogen (20.2%), of which 13.8 m. eq. (4.6%) was in the form of volatile bases. After evaporation, the residue was extracted with chloroform (to remove trimethylamine hydrochloride), warmed with alcoholic hydrogen chloride in order to form ethyl esters, concentrated and extracted with ether. The ethereal solution on evaporation left 0.2–0.3 g. of a residue which contained 0.8 m. eq. of (non-basic) nitrogen. The ether-insoluble portion was rendered alkaline with potassium carbonate solution and extracted with ether, which took up slightly less than 1 g. of a product containing 9.0 m. eq. of (basic) nitrogen. The watery solution contained 48.9 m. eq. of nitrogen.

Alanine and Formaldehyde.—(1) A mixture of 8.9 g. (0.1 mole) of alanine, 15 cc. of 90% formic acid and 10 cc. of formalin was heated under reflux on the steam-bath. Rapid evolution of carbon dioxide occurred. After two hours, 10 cc. of concentrated hydrochloric acid was added, and the mixture was evaporated to dryness. The dark brown, sirupy residue, which contained 11.0 m. eq. of trimethylamine and 85.7 m. eq. of non-volatile nitrogen, was esterified by alcoholic hydrogen chloride and subjected to ether extraction from acid and alkaline solution. The ether extract from acid solution (wt. 0.1 g.) contained 0.3 m. eq. N; that after adding potassium carbonate (wt. 1 g.) contained 4.6 m. eq. N; the residual alkaline solution contained 91.0 m. eq N. The bases extracted by ether distilled over a wide range, mainly above 220°, with decomposition.

(2) A mixture of 17.8 g. (0.2 mole) of alanine, 80 cc. of acetic acid and 36 cc. of formalin was boiled under reflux for twenty minutes; the light brown solution was treated with 100 cc. of *N* sulfuric acid and evaporated to dryness under reduced pressure. The brown, amorphous residue was dissolved in 250 cc. of water, made alkaline with 100 g. of crystallized barium hydroxide, and distilled into standard acid. The volatile bases amounted to 14.9 m. eq.; these were found to consist of 2.34 m. eq. of ammonia, 8.56 m. eq. of methylamine, and 3.93 m. eq. of di- and trimethylamine. The residual alkaline solution was diluted, freed of barium hydroxide with carbon dioxide, concentrated, filtered and treated with 800 cc. of absolute alcohol. The precipitate was redissolved in water and reprecipitated with alcohol. After drying it weighed 7.2 g.; it contained 5.8% of nitrogen and 20.2% of barium.

β-Dimethylaminopropionic Acid Hydrochloride.—A mixture of 3.56 g. of β-aminopropionic acid, 25 cc. of 90% formic acid and 5 cc. of formalin was boiled under reflux for eight hours, treated with 5 cc. of concentrated hydrochloric acid, and evaporated to complete dryness. The crystalline residue was washed with 10–15 cc. of glacial acetic acid, which removed a viscous by-product. The yield of colorless crystals, which melted at 188–191° (uncorr), was 2.3 g. (38% of the calculated amount).

(30) Excess of silver oxide must be avoided as it rapidly oxidizes the dimethylglycine to carbon dioxide and dimethylamine, even in the cold.

(31) Willstätter, *Ber.*, **35**, 599 (1902).

Anal. Calcd. for $C_5H_{12}O_2NCl$: C, 39.0; H, 7.16; N, 9.12; Cl, 23.8. Found: C, 39.4; H, 7.74; N, 8.81; Cl, 22.4.

α-Dimethylamino-isobutyric Acid Hydrochloride.—A mixture of 5.15 g. (0.05 mole) of α-aminoisobutyric acid, 13 cc. of 90% formic acid and 10 cc. of formalin was gently warmed under reflux. At 68°, evolution of gas began; it ceased after one and one-half hours, when the temperature had risen to 107°. After two hours 6 cc. of concentrated hydrochloric acid was added and the mixture was evaporated to dryness at 90–100°. The crystalline residue was recrystallized from acetic acid; in all 6.65 g. (80% of the calculated amount) of colorless needles was secured. The product is the hydrochloride of α-dimethylaminoisobutyric acid.

Anal. Calcd. for $C_6H_{14}O_2NCl$: N, 8.36; Cl, 21.2. Found: N, 8.30, 8.10; Cl, 21.1, 21.0.

It melts with decomposition at 264° (uncorr.), is readily soluble in water, alcohol and boiling acetic acid, sparingly in cold acetic acid, but insoluble in acetone or chloroform. A similar experiment with 25.75 g. of the amino acid gave a yield of 30.0 g. (72%) of the hydrochloride.

No attempt was made to prepare the free dimethylamino acid. After long boiling with methyl alcoholic hydrogen chloride, the bulk of the original hydrochloride crystallized out unchanged; the mother liquor, on treatment with ether and saturated potassium carbonate solution, furnished a small yield (20–25%) of the methyl ester, b. p. 154–155°. This is a colorless liquid, miscible with water but insoluble in concentrated potassium carbonate.

Anal. Calcd. for $C_7H_{15}O_2N$: N, 9.66. Found: N, 9.70.

α-Dimethylamino-α-phenylbutyric Acid.—A mixture of 0.90 g. of α-amino-α-phenylbutyric acid,[32] 2 cc. of formic acid and 1 cc. of formalin was boiled for forty minutes, cooled and diluted with 5 cc. of water, which caused the separation of 0.29 cc. of a neutral oil, identified as propiophenone by its semicarbazone m. p. 176–178° (uncorr.). The residual solution was evaporated and treated with acetone. The resulting needles, weighing 0.75 g., melted with decomposition at 220° (uncorr.) and were readily soluble in cold water and alcohol but insoluble in acetone.

Anal. Calcd. for $C_{12}H_{17}O_2N$: C, 69.6; H, 8.22; N, 6.77. Found: C, 69.6; H, 8.37; N, 6.57.

The mother liquor gave a 16.4% yield of volatile bases.

α-Aminophenylacetic Acid and Formaldehyde.—A mixture of 5.0 g. of α-aminophenylacetic acid, 50 cc. of acetic acid, and 5 cc. of formalin was boiled for eight hours and then distilled in a current of steam. The benzaldehyde in the distillate yielded 0.5 g. (7.6%) of the phenylhydrazone. The residual solution contained 18.1% of the original nitrogen in the form of volatile bases having the following distribution (determined by the method outlined for hexamethylenetetramine): NH_3, 6.7; CH_3NH_2,[33] 46.6; $(CH_3)_2NH$, 39.4; $(CH_3)_3N$, 7.2.

Phenylalanine and Formaldehyde.—(1) A mixture of 3.3 g. of *dl*-phenylalanine, 10 cc. of 90% formic acid and 2 cc. of formalin was warmed on the steam-bath for fifteen minutes. Carbon dioxide was rapidly evolved; separation of crystals occasionally occurred. The reaction mixture was cooled and diluted with 2 cc. of water; the crystalline product was collected, washed with 5 cc. of cold alcohol, and recrystallized from 50 cc. of hot alcohol. A further small quantity was obtained from the mother liquors. The total yield was 2.2 g. of colorless hexagons or needles which melted at 245–246° (uncorr.).

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(32) The authors are indebted to Dr. R. M. Herbst for this substance.

(33) This fraction included traces of other bases possessing hydrochlorides insoluble in chloroform; it melted at 210–213° (12° lower than pure methylamine hydrochloride).

Anal. Calcd. for $C_{19}H_{17}O_4N$: C, 70.59; H, 5.27; N, 4.34; mol. wt., 323. Found (different samples): C, 70.70, 70.65, 70.63, 70.47, 70.45; H, 5.47, 5.44, 5.42, 5.24, 5.25; N, 4.30, 4.42, 4.65; mol. wt. (in camphor), 319.

The combined mother liquor from several such preparations was rendered alkaline and distilled; the volatile bases consisted entirely of methylamine hydrochloride which melted at 222–227° and showed no depression when mixed with an authentic sample.

(2) A solution of 3.3 g. of *l*-phenylalanine[34] (which had $[\alpha]^{20}_{D}$ −11.7° in water, and was therefore more than two-thirds racemized) in 12.5 cc. of formic acid and 2 cc. of formalin was heated for one hour on the steam-bath, and the product (2.1 g.) isolated as above. It melted at 250–251° (uncorr.) and, apart from its optical activity, appeared to be identical with the product from *dl*-phenylalanine.

Rotation. $[\alpha]^{20}_{D}$ −37.6° (2.7% in *N* NaOH).

(3) To a suspension of 3.3 g. of *dl*-phenylalanine in 13 cc. of acetic acid was added 2 cc. of formalin. Solution took place readily in the cold. On boiling for one hour, no apparent evolution of gas occurred; the acetic acid was evaporated under reduced pressure and the residue recrystallized from alcohol; yield 1.00 g., m. p. 246°; m. p. of mixture with sample prepared in formic acid, 245°.

Anal. Found: C, 70.64; H, 5.58; N, 4.37; mol. wt. (in camphor), 336.

The mother liquor contained 3.7 m. eq. of volatile base, of which 3.3 m. eq. consisted of methylamine (hydrochloride m. p. 225°) and 0.4 m. eq. of di- and trimethylamines.

(4) A solution of 1.65 g. of *dl*-phenylalanine, 0.83 g. of phenylpyruvic acid and 1 cc. of formalin in 13 cc. of acetic acid was boiled under reflux for one hour. The acetic acid was evaporated under reduced pressure, and the residue crystallized from alcohol. The weight of the crude product was 1.00 g.; after one recrystallization it melted at 245°, and was identical with preparations from phenylalanine alone. The mother liquors contained 1.03 m. eq. of volatile base, which comprised 19% of ammonia, 77% of methylamine and 4% of di- and trimethylamines.

Di-*p*-methoxy Derivative of $C_{19}H_{17}O_4N$.—To a warm solution of 7.0 g. of *l*-*p*-methoxyphenylalanine in 15 cc. of formic acid was added 4 cc. of formalin. Evolution of gas occurred at once. After being boiled under reflux for one hour, the mixture was diluted with an equal volume of alcohol and evaporated to 20 cc. The crystalline product was collected and washed with cold alcohol; it weighed 1.2 g. and melted at 217–218°. After two recrystallizations from absolute alcohol it was obtained as prisms which melted sharply, with decomposition, at 231°. In general properties it closely resembled the product obtained from phenylalanine. Several preparations were analyzed.

Anal. Calcd. for $C_{21}H_{21}O_6N$: C, 65.8; H, 5.48; N, 3.66; OCH_3, 16.19. Found: C, 66.0, 65.7, 66.0, 65.8; H, 5.69, 5.66, 5.41, 5.31; N, 3.85, 3.72; OCH_3, 16.00.

Rotation. $[\alpha]^{21}_{D}$ −31.0° (3.6% in *N* NaOH).

The filtrate from the crystals gave a 25% yield of volatile bases having nitrogen distribution: NH_3, 0; CH_3NH_2, 73; $(CH_3)_2NH$, 28; $(CH_3)_3N$, 5.

Mono-*p*-methoxy Derivative of $C_{19}H_{17}O_4N$.—A solution of 3.24 g. of *l*-*p*-methoxyphenylalanine, 2.74 g. of phenylpyruvic acid and 1.2 cc. of formalin in 20 cc. of acetic acid was boiled under reflux for one hour. To the cold mixture was added 1.6 cc. of concentrated hydrochloric acid, and the crystalline product (3.35 g.) washed first with a little cold acetic acid and then with alcohol, and recrystallized from absolute alcohol. It then melted at 239–240°; its general properties were almost identical with those of $C_{19}H_{17}O_4N$.

Anal. Calcd. for $C_{20}H_{19}O_5N$: C, 68.0; H, 5.38; N, 3.97; OCH_3, 8.78. Found: C, 67.9; H, 5.68; N, 4.44; OCH_3, 8.81.

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(34) A sample of protein origin, generously presented by Dr. H. B. Vickery.

Rotation. $[\alpha]^{21.5}_{D}$ −135.5° (3.6% in *N* NaOH).

The mother liquor gave a 3.6% yield of volatile bases, of which one-third consisted of ammonia.

Constitution of $C_{19}H_{17}O_4N$

The compound is insoluble in water and in dilute acids; it readily dissolves in cold concentrated sulfuric acid, from which it is precipitated unchanged on dilution. It is soluble in ammonia and in dilute alkalies (1 equivalent of 0.1 *N*) or alkali carbonate solutions. It is moderately soluble in acetic acid and acetone, less so in alcohol, and almost insoluble in ether, benzene and carbon tetrachloride. An alcoholic solution yields an intense blue-green color with ferric chloride.

Barium Salt.—On attempting to determine the neutral equivalent, employing phenolphthalein as indicator, indefinite end-points were obtained on titration with sodium hydroxide in water solution. They were somewhat sharper in alcohol, but the observed neutral equivalents varied with the composition of the solvent; 210 in 25% alcohol, 188 in 80% alcohol. A satisfactory end-point was secured by titrating the compound in alcohol with barium hydroxide, when the barium salt precipitated; a neutral equivalent of 165.5 (calcd. 161.5) was found in this way. The barium salt (microscopic plates) was collected, washed with alcohol and dried at 100°.

Anal. Calcd. for $C_{19}H_{15}O_4NBa \cdot 3H_2O$: C, 44.5; H, 4.10; Ba, 26.7. Found: C, 44.4; H, 4.05; Ba, 26.8.

No loss of weight occurred at 115° (sixteen hours); at 150° decomposition took place, but only 2.17% was lost in three hours.

A flocculent, alcohol-soluble silver salt was precipitated on adding silver nitrate to a solution of the ammonium salt, but this rapidly decomposed, even in the dark, with formation of metallic silver and an odor of phenylacetaldehyde.

Absence of Basic Properties.—No reaction was observed in acetone or alcohol solution with alcoholic hydrochloric acid, employing benzene-azo-α-naphthylamine as indicator. The compound formed no platinichloride, and was recovered unchanged after treatment in alkaline solution with phenyl isocyanate. It yielded no nitrogen on treatment with sodium nitrite and acetic acid.

Decarboxylation.—A 0.500-g. sample, heated at 255° in a current of hydrogen, evolved 0.068 g. of carbon dioxide, together with 0.016 g. of moisture (calcd. for loss of one COOH: CO_2, 0.0678 g.).

Oxidation.—The compound is readily oxidized by cold, alkaline permanganate: a solution of 0.0808 g. in 5 cc. of 0.1 *N* sodium hydroxide required 30.5 cc. of 0.1 *N* potassium permanganate. The only product obtained was impure benzoic acid (m. p. 98°) which gave a green color with alcoholic ferric chloride (suggesting the presence of phenylpyruvic acid). No volatile base was formed.

Permanganate in acetone, and alkaline hypobromite are readily reduced, but bromine in acetic acid is only slowly decolorized and Fehling's solution is without action. Profound oxidation occurs on heating in water with silver oxide: 0.0808 g. of the compound, boiled with a water suspension of the freshly precipitated and washed oxide from 2 g. of silver nitrate, yielded 0.0612 g. of carbon dioxide (calcd., 0.055 g.). In a similar experiment with 4.98 g. (15.4 millimoles) of the compound and the oxide from 45 g. of silver nitrate, the volatile base amounted to 5.45 m. eq. and consisted entirely of ammonia.[35] The residual solution contained 1.95 m. eq. of non-volatile nitrogen; the remaining 52% was not accounted for. Benzaldehyde (identified as the phenylhydra-

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(35) An investigation, in progress in this Laboratory, of the action of silver oxide upon amino acids indicates that N-alkyl derivatives of such acids yield, under these conditions, all of their nitrogen in the form of the corresponding alkylamine. In this case, therefore, no methyl group appears to be attached to the nitrogen atom.

zone m. p. 156–158°) was formed in small amount. The reduced silver amounted to 250 m. eq., or 90% of the quantity calculated from the equation: $C_{19}H_{17}O_4N + 9Ag_2O = 2C_6H_5CHO + 5CO_2 + NH_3 + H_2O + 18Ag$.

Hydrogen peroxide oxidized the compound: a solution of 1.00 g. (3.09 millimoles) in 16 cc. of 0.5 *N* sodium hydroxide was treated with 10 cc. of 30% hydrogen peroxide. After twenty-four hours at room temperature the mixture was acidified and extracted with ether. The extracted acids were redissolved in alkali and precipitated from a volume of 15–20 cc.; the resulting crystals melted at 122° and did not depress the melting point of pure benzoic acid. The filtrate from the benzoic acid had the odor of phenylacetic acid; it was not found possible to isolate this product, but further evidence for its presence was secured by distilling out the volatile acids (0.59 m. eq.) and boiling the distillate with silver oxide (from 2.5 g. of silver nitrate) for five hours. The odor of phenylacetic acid had then disappeared, and 0.96 m. eq. of metallic silver had formed. This corresponds to the oxidation of 0.16 m. eq. of phenylacetic acid[36] to benzoic acid.

Alkaline Fusion.—On fusion with alkali, ammonia is evolved, together with vapors having the odor of styrene. In a typical experiment a mixture of 0.529 g. (1.63 millimoles) of the compound, 2 g. of powdered potassium hydroxide and 0.5 cc. of a 40% solution of sodium hydroxide was heated by an oil-bath in a platinum crucible enclosed in a glass tube through which a slow current of nitrogen was passed. The issuing vapors were led through a trap surrounded by solid carbon dioxide in alcohol (to condense any styrene), and then into dilute acid. The bath was held at 280–285° for three hours. The contents of the chilled tube were treated with dilute sulfuric acid and extracted with five 10-cc. portions of chloroform. The acid layer was joined with that in the absorption vessel and the volatile base determined in the regular way. It amounted to 1.02 m. eq. (65% of the calculated quantity) and consisted almost entirely of ammonia. The chloroform layer was treated with a slight excess of bromine and evaporated at room temperature, when yellow crystals were obtained which melted at 68–70° (styrene dibromide melts at 73°). The residue in the crucible was rapidly dissolved in water and the solution acidified, when 0.2305 g. of carbon dioxide was evolved. This is 107% of the amount of carbon dioxide calculated from the equation:[37] $C_{19}H_{17}O_4N + 6KOH = 2C_8H_8 + NH_3 + 3K_2CO_3 + H_2O + H_2$. The acid solution remaining after the expulsion of the carbon dioxide contained a small amount of a black precipitate, but no acids extractable by ether.

Acetylation.—The compound was recovered unchanged after being boiled for forty hours with 10 parts of anhydrous formic acid—evidence of the absence of alcoholic hydroxyl groups. On the other hand, though insoluble in cold acetic anhydride, it slowly dissolves on warming, and then fails to separate on cooling. Such a solution, prepared from 0.3 g. in 3 cc. of anhydride, was allowed to evaporate in a vacuum desiccator over solid potassium hydroxide. The rather sticky, crystalline residue was recrystallized from a mixture of ethylene chloride (in which it was very soluble) and benzene (which dissolved it only sparingly), when it was obtained in the form of long, thin needles which melted at 192–194° (uncorr.). From its analysis it appears to be an internal anhydride of a monoacetyl derivative.

Anal. Calcd. for $C_{21}H_{17}O_4N$: C, 72.7; H, 4.90; N, 4.04. Found: C, 73.5; H, 5.20; N, 3.79.

A suspension of 68.0 mg. in 8 cc. of acetone was titrated with 0.1 *N* sodium hydroxide in the cold, employing phenolphthalein. When 3.3 cc. had been added, solution was complete and the pink color appeared. This soon faded on warming. The titration

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(36) Unpublished results of experiments by Dr. R. M. Herbst in this Laboratory indicate the approximate correctness of this interpretation.

(37) The reaction with alkali probably involved not only decarboxylation but oxidation of the type studied by Fry and collaborators [This Journal, 46, 2268 (1924); 48, 958 (1926); 50, 1122 (1928)].

was continued until a permanent end-point had been reached; this occurred with 6.3 cc. of the alkali, whence the saponification equivalent was 108 (calcd., 116). The acetone was then evaporated and the residual solution acidified; the precipitate was washed with water, then with alcohol and dried. It melted at 247–248°, and obviously consisted of the original compound, $C_{19}H_{17}O_4N$.

Benzoylation.—An apparently hydrated benzoyl derivative was prepared by shaking a solution of 1.0 g. of the compound in 20 cc. of 4 *N* sodium hydroxide with 6 cc. of benzoyl chloride in two portions. The resulting solution was acidified with 5 cc. of acetic acid, the granular precipitate was filtered off at once and repeatedly extracted with warm ligroin. The heavy, pale yellow, insoluble sirup was dissolved in ethylene chloride, and the filtered solution concentrated to 3 cc. On treatment with 15 cc. of ligroin an oil was precipitated; this was washed with petroleum ether and dried *in vacuo* over phosphorus pentoxide. A friable resin weighing 1.45 g. remained. It melted at 60° after softening at a lower temperature.

Anal. Calcd. for $C_{26}H_{23}O_6N$: C, 70.2; H, 5.17; N, 3.15. Found: C, 70.4; H, 5.8; N, 2.94.

The product is readily soluble in alcohol; on adding a few drops of dilute alkali to the solution, the odor of ethyl benzoate is developed at once in the cold. The saponification equivalent, determined in the same way as described for the acetyl derivative, was 146.5 (calcd., 148.3). On acidifying after titration, the original acid was regenerated, m. p. 249° after recrystallization from acetone.

Methyl Ester.—On esterification by methyl alcoholic hydrogen chloride, only one alkyl group enters the molecule; the product consisted of prisms of m. p. 118°.

Anal. Calcd. for $C_{20}H_{19}O_4N$: C, 71.2; H, 5.64; N, 4.15; OCH_3, 9.19. Found: C, 71.3; H, 5.78; N, 4.30; OCH_3, 9.16.

This derivative gave the blue-green color with alcoholic ferric chloride. On titrating a cold solution in methyl alcohol with barium hydroxide, employing phenolphthalein, a neutral equivalent of 326 (calcd., 337) was obtained. No precipitate was formed until an excess of barium hydroxide was added and the mixture had been boiled. Titration of the excess of baryta after two hours of heating gave a saponification equivalent of 154 (calcd., 161.5).

Methyl Ether.—To a solution of 1.0 g. of the compound in 7 cc. of *N* sodium hydroxide was added, in several portions and with vigorous shaking, 1 cc. of methyl sulfate, further additions of sodium hydroxide being made so as to maintain alkalinity to litmus. A gummy precipitate formed; when the reaction was complete, the clear supernatant solution was decanted and acidified with hydrochloric acid. The amorphous precipitate was collected, washed with water, and dissolved in a small amount of methyl alcohol; the solution was allowed to evaporate over sulfuric acid. The amorphous residue, which melted rather indefinitely at 75–90°, was very soluble in methyl alcohol. With alcoholic ferric chloride, only a pale yellow color developed, indicating the methylation of an enolic hydroxyl group.

The barium salt of the methyl ether was precipitated on adding an excess of 0.4 *N* barium hydroxide to a solution of 0.5 g. of the ether in 5 cc. of cold methyl alcohol. It is insoluble in alcohol, but somewhat soluble in hot water, from which it separates in gelatinous form on cooling.

Anal. Calcd. for $(C_{20}H_{18}O_4N)_2Ba$: C, 59.3; H, 4.45; Ba, 16.95; OCH_3, 7.68. Found: C, 59.2; H, 4.43; Ba, 16.93; OCH_3, 7.69.

The anilide was prepared by heating 0.3 g. of the methyl ether with 1.5 cc. of aniline for two minutes and then distilling off the bulk of the excess aniline under reduced pressure. The oily residue was washed with dilute acetic acid and dissolved in methyl alcohol, from which it separated in rectangular prisms melting at 208° (uncorr.).

Anal. Calcd. for $C_{26}H_{25}O_3N_2$: N, 6.78; OCH_3, 7.51. Found: N, 6.58; OCH_3, 7.23.

Methyl Ester of Methyl Ether.—The gummy precipitate formed by the action of methyl sulfate and alkali was dissolved in a small volume of methyl alcohol and an equal volume of water was slowly added to the filtered solution. The product separated as an oil which rapidly crystallized; yield, 0.5 g. of prisms melting at 78°.

Anal. Calcd. for $C_{21}H_{21}O_4N$: C, 71.8; H, 5.98; N, 3.98; OCH_3, 17.66; sapon. eq., 351. Found: C, 71.6; H, 6.03; N, 4.10; OCH_3, 16.77, 16.83; sapon. eq., 357.

An alcoholic solution gave only a pale yellow color with ferric chloride. The solution obtained after saponification gave, on acidification, a product identical with the above methyl ether.

Anilide of Anil.—A suspension of 1.0 g. of $C_{19}H_{17}O_4N$ in 3 cc. of aniline was gently heated over the flame; before the boiling point of aniline was reached, solution suddenly took place with evolution of steam. After being boiled under reflux for twenty minutes the mixture was allowed to cool, and the product which separated was recrystallized from acetone; yield, 0.9 g. of prismatic needles which melt without decomposition at 215° (uncorr.).

Anal. Calcd. for $C_{31}H_{27}O_2N_3$: C, 78.6; H, 5.71; N, 8.86. Found: C, 78.9; H, 5.82; N, 9.33.

This derivative is insoluble in alkali and gives no color with ferric chloride.

Reduction of Carbonyl.—Treatment of the compound with hydrogen under pressure and an active palladium, or platinum oxide, catalyst was without effect when 0.1 *N* sodium hydroxide (2 equivalents) was employed as a solvent,[38] nor did reduction occur on treating an alkaline solution with sodium amalgam. Boiling with red phosphorus in a mixture of hydriodic acid and acetic anhydride led to the formation of tarry products only. A solution in acetic anhydride failed to respond to catalytic hydrogenation, using palladium; the crystalline product, after hydrolysis by alkali, yielded only the starting material.

However, zinc dust in acetic acid, with which Borsche reduced triphenylpyrrolidinedione,[39] brings about the desired reduction, yielding a product which neither crystallized nor yielded a crystalline barium salt. It was not analyzed, for as it gave no color with ferric chloride, there was no question as to its identity.

Hydroxylamine Derivative.—On treatment in dilute acetic acid with phenylhydrazine, *p*-nitrophenylhydrazine and semicarbazide, no reaction occurred, and unchanged material was recovered. A new compound, however, was formed with hydroxylamine: to a solution of 0.5 g. of the acid in 4 cc. of *N* sodium hydroxide was added 0.2 g. of hydroxylamine hydrochloride. An oily precipitate formed and soon became crystalline. Solution occurred on heating to 100°; 0.2 cc. of glacial acetic acid was added, and the oily precipitate stirred until it had completely crystallized. It melted with decomposition at 185–186°, after becoming yellow above 160°. It was dried at 100° for analysis.

Anal. Calcd. for $C_{19}H_{18}O_4N_2$: C, 67.5; H, 5.33; N, 8.29. Found: C, 67.8; H, 5.58; N, 7.67.

This substance is appreciably soluble in cold water, readily in hot water and in alcohol. Although its analytical figures are in reasonable accord with those calculated for an oxime, its general properties indicate a less stable type of compound, in which the enolic character persists. It gives a blue-green color with ferric chloride in alcohol and readily reduces Fehling's solution. On adding, in small portions, an equal volume of *N* hydrochloric acid to a cold, concentrated alcoholic solution, the original acid (m. p. 246° dec.) crystallizes.

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[38] In a control experiment with the palladium catalyst under the same conditions, α-benzoylaminocinnamic acid was smoothly reduced to benzoylphenylalanine, m. p. 182–183°.

[39] Borsche, *Ber.*, **42**, 4077 (1909).

Summary

Simple aliphatic amines are smoothly methylated to the corresponding tertiary amines by warming in formic acid solution with formaldehyde. Dibenzylamine, under these conditions, is mainly converted into methyldibenzylamine, but at the same time yields some benzaldehyde and a more volatile base (probably dimethylbenzylamine).

Tetra-alkyl-diaminomethanes, on warming with formic acid, are converted into equimolar quantities of the corresponding dialkylamine and methyldialkylamine. Hexamethylenetetramine reacts with warm formic acid yielding mainly ammonia and trimethylamine, with smaller amounts of mono- and dimethylamines; only three-quarters of the methylene carbon reappears as methyl in the final mixture.

Only about two-thirds of the anticipated amount of carbon dioxide, calculated on the assumption that the formic acid is the sole hydrogen donor, is obtained in these reactions; apparently some of the formaldehyde also contributes hydrogen.

Amino acids react with formaldehyde in warm formic or acetic acid with detachment of some of the nitrogen in the form of volatile bases. Dimethyl derivatives were isolated from the reaction in formic acid with glycine, β-aminopropionic acid, α-aminoisobutyric acid and α-amino-α-phenylbutyric acid. Other amino acids yielded breakdown and condensation products of various degrees of complexity. Benzaldehyde was isolated from α-aminophenylacetic acid, propiophenone from α-amino-α-phenylbutyric acid, and α-(4-phenyl-2,3-diketopyrrolidyl)-β-phenylpropionic acid from phenylalanine. Mechanisms by which these products may be formed are suggested.

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Studies in Thiophenol Chemistry. I. A Condensation Reaction between Thiophenols and Condensed Aldehyde-Ammonias[1]

BY GREGG DOUGHERTY AND WENDELL H. TAYLOR[2]

In connection with a study of the condensation of thiophenol and formaldehyde under a variety of conditions, it was found that this mercaptan readily condenses with hexamethylenetetramine and several other hydramides, ammonia being evolved. This work has already been mentioned in a brief communication[3] and it is now desired to present a more detailed account of the several reactions and their products.

Hexamethylenetetramine and Thiophenols.—It has long been known that hexamethylenetetramine reacts with certain weakly acidic compounds according to the general equation

$$(CH_2)_6N_4 + 6HR \longrightarrow 2N(CH_2R)_3 + 2NH_3 \qquad (1)$$

where, for example, R may be $-CN$,[4] C_6H_5CONH-,[5] or $CH_3N(NO_2)-$.[6] Stronger acids generally cause complete decomposition of the base, and phenols, which first form addition compounds, finally yield resinous substances[7] when heated with hexamethylenetetramine.

It is therefore interesting that thiophenol and various substituted thiophenols should yield condensation products exactly of the type $N(CH_2R)_3$. Thus, in reaction (1), R may be $—SC_6H_5$, $—SC_6H_4Br$, $—SC_6H_4NO_2$, $—SC_6H_4CH_3$ (the last three para substituted) or even $—SCH_2C_6H_5$.

The reaction is easily brought about by refluxing the reactants in an inert solvent such as 1,4-dioxane, and its course may be followed by determining the amount of ammonia evolved. By this means the reaction in the case of hexamethylenetetramine and thiophenol has been shown to be

$$(CH_2)_6N_4 + 6C_6H_5SH \longrightarrow 2N(CH_2SC_6H_5)_3 + 2NH_3 \qquad (2)$$

The triphenylmercaptomethylamine structure of the product is substantiated by analyses and molecular weight determinations, and by quantitative hydrolysis experiments in which the following reaction takes place

$$N(CH_2SC_6H_5)_3 + 3HOH \xrightarrow{HCl} NH_3 + 3C_6H_5SH + 3HCHO \qquad (3)$$

The intermediate formation of $N(CH_2OH)_3$ may be presumed; the final products weighed are ammonium chloride and formaldehyde-diphenylmercaptal.[8]

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(1) The material of this paper is from the dissertation of Wendell H. Taylor, presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Princeton University, 1933.

(2) Charlotte Elizabeth Procter Fellow, 1931–1932.

(3) Dougherty and Taylor, THIS JOURNAL, **55**, 1294 (1933).

(4) Eschweiler, *Ann.*, **278**, 230 (1894).

(5) Descudé, *Ann. chim. phys.*, [7] **29**, 541 (1903).

(6) Franchimont, *Rec. trav. chim.*, **29**, 355 (1910).

(7) Redman, Weith and Brock, *Ind. Eng. Chem.*, **6**, 3 (1914). Scheiber and Sändig, "Artificial Resins," Pitman, London, 1931, p. 302

It may be pointed out in passing that the reaction postulated here (2) is much more readily explained on the basis of a symmetrical hexamethylenetetramine molecule containing four equivalent nitrogen atoms than upon the assumption of the Lösekann formula, $N(CH_2N{=}CH_2)_3$, still occasionally advocated.[9] x-Ray analysis of the hexamethylenetetramine crystal[10] so strongly indicates the tetrahedral structure of the molecule that only the most positive chemical evidence may now be considered admissible in favor of the old formula.

Hydrobenzamide and Thiophenols.—Hydrobenzamide, $(C_6H_5CH{=}N)_2CHC_6H_5$, more properly named tribenzylidenediamine, is a condensed aldehyde-ammonia or "hydramide." Whether it is regarded merely as a secondary condensation product of benzaldehyde and ammonia, or as an aldehyde of the "ammonia system,"[11] its close relationship to hexamethylenetetramine is evident.

The ready hydrolysis of hydrobenzamide by acids into benzaldehyde and ammonia is a characteristic reaction, but its stepwise decomposition by weak acids, as in the case of hexamethylenetetramine, has not hitherto been known. It has been found that thiophenol and various substituted thiophenols, as well as benzyl mercaptan, cause such a partial decomposition, which may be looked upon as the formation of a half-mercaptal. Thus

$$2(C_6H_5CH{=}N)_2CHC_6H_5 + 3RSH \longrightarrow 3C_6H_5CH{=}NCH(SR)C_6H_5 + NH_3 \qquad (4)$$

It may well be that the first stage in the reaction is the formation of benzylidene-imine, a substance recently found[11] to be capable of existence in the free state.

$$(C_6H_5CH{=}N)_2CHC_6H_5 + RSH \longrightarrow C_6H_5CH{=}NCH(SR)C_6H_5 + C_6H_5CH{=}NH \qquad (5)$$

Two molecules of benzylidene-imine formed in this way might then react with the third molecule of mercaptan, giving ammonia and the third molecule of the half-mercaptal

$$RSH + 2C_6H_5CH{=}NH \longrightarrow C_6H_5CH{=}NCH(SR)C_6H_5 + NH_3 \qquad (6)$$

In any case, the stoichiometric equation for the reaction may be represented by (4). This has been established by quantitative estimation of the evolved ammonia, and by analyses and molecular weight determinations on the products. The latter are well-crystallized, colorless solids, obtained in nearly quantitative yield when the condensation is carried out in boiling 1,4-dioxane solution. The half-mercaptal structure assigned to them appears to be confirmed by the results of quantitative hydrolysis experiments; thus

$$C_6H_5CH{=}NCH(SC_6H_5)C_6H_5 + HOH \longrightarrow 2C_6H_5CHO + C_6H_5SH + NH_3 \qquad (7)$$

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[8] Formed from the thiophenol and excess formaldehyde in the presence of dry hydrogen chloride.

[9] Marotta and Alessandrini, *Gazz. chim. ital.*, **59**, 942 (1929); **61**, 977 (1931).

[10] Dickinson and Raymond, THIS JOURNAL, **45**, 23 (1923).

[11] Strain, *ibid.*, **49**, 1558 (1927).

The benzaldehyde may be weighed as the phenylhydrazone; the thiophenol as lead phenyl mercaptide; the ammonia as ammonium chloride.

Extension to Other Hydramides and Mercaptans.—The same type of condensation has been found to take place with such substituted hydrobenzamides as 3,3′,3″-trinitrohydrobenzamide and hydro-*p*-toluamide, and with hydrofurfuramide; in these cases only the reaction with thiophenol was investigated. Preliminary work has shown that it may be possible to extend this reaction to the simple aliphatic mercaptans. *n*-Amyl mercaptan—the only one studied thus far—undergoes slow reaction with both hexamethylenetetramine and hydrobenzamide, ammonia being evolved. In neither case, however, has a crystalline product yet been obtained.

General Nature of the Products.—The products from all these reactions are very similar in physical and chemical properties. They are nearly all colorless, odorless, crystalline[12] solids of fairly low melting point; they are readily soluble in most organic solvents but only sparingly so in cold alcohol and in petroleum ether.

In alcohol solution they give no immediate precipitate when alcoholic lead acetate is added, but on warming, or on addition of a little acid, a mercaptide precipitate soon forms. They are much less easily hydrolyzed by alkalies than are the substituted trimethylamines obtained from hexamethylenetetramine and hydrogen cyanide.

The solid members of this group melt sharply without decomposition, but may not be distilled, even under greatly reduced pressure. Thus, triphenylmercaptomethylamine gives large amounts of diphenyl disulfide upon attempted distillation at 1 mm. pressure; the nature of any other pyrolytic products has not been determined.

Attempts to prepare simple derivatives, such as sulfones, have not been successful. Because of the ease with which these compounds are hydrolyzed by acids, neutral or alkaline oxidizing agents must be employed. However, dilute alkaline potassium permanganate may be boiled for several hours with benzalphenylmercaptobenzylamine, $C_6H_5CH{=}NCH(SC_6H_5)C_6H_5$, with little effect; while 30% hydrogen peroxide in glacial acetic acid solution brings about complete decomposition, with formation of benzoic acid. Bromine in dilute ether solution is rapidly decolorized by benzalphenylmercaptobenzylamine but the molecule is completely broken up and diphenyl disulfide can be isolated from the solution as the chief product.

Experimental Part

Materials Used.—Thiophenol, *p*-thiocresol, thio-β-naphthol, benzyl mercaptan and *n*-amyl mercaptan were obtained from the Eastman Kodak Company. *p*-Bromothiophenol was prepared by reduction with zinc and hydrochloric acid of 4,4′-dibromodiphenyl disulfide, the latter being obtained by direct bromination[13] of diphenyl disulfide. *p*-Nitrothiophenol was made by the action of alcoholic potassium hydrosulfide upon *p*-nitrochlorobenzene.[14]

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[12] The only products not obtained crystalline are those from hexamethylenetetramine with thiophenol or thio-β-naphthol.

The hexamethylenetetramine used was Merck U. S. P. "Formin." Hydrobenzamide was prepared by shaking strong aqueous ammonia with pure benzaldehyde. The product was always recrystallized before use. 3,3′,3″-Trinitrohydrobenzamide was made by the method of Fürth,[15] while hydro-*p*-toluamide and hydrofurfuramide were obtained by direct condensation of aqueous alcoholic ammonia with *p*-tolualdehyde and furfuraldehyde, respectively.

Commercial dioxane was twice treated with sodium wire and redistilled, the fraction boiling at 101–102° (760 mm.) being retained. Removal of chlorinated compounds is essential, since in their presence hexamethylenetetramine hydrochloride is sometimes formed; oxidation of certain thiophenols to disulfides has also been observed in dioxane containing chlorine compounds.

Apparatus.—The condensations of thiophenols with the various hydramides were carried out in a 150-cc. side-neck Erlenmeyer flask provided with a long vertical spiral condenser. A slow current of dry air (in some runs, nitrogen) was passed into the side-neck of the flask while the dioxane solution of the reactants was gently refluxed; this carried the evolved ammonia through the condenser into a receiver containing an excess of standard hydrochloric acid. By determining the acid left in the receiver after ammonia was no longer given off,[16] the course and nature of the reaction could be studied.

Analyses for carbon, hydrogen and nitrogen were carried out by the micro methods of F. Pregl; halogens and sulfur were determined by a semi-micro method using the micro-balance and small fritted glass filter crucibles, following in general the usual Carius technique.

Molecular weights were determined either by the familiar freezing point method of Beckmann, or with the very convenient boiling point apparatus designed by Rieche.[17] The solvents used are designated later.

Hexamethylenetetramine and Thiophenol.—One and four-tenths grams (0.01 mole) of hexamethylenetetramine and 3.24 g. (nearly 0.03 mole) of thiophenol were mixed with 20 cc. of 1,4-dioxane and refluxed for twenty-three hours in the apparatus described above. The evolved ammonia was determined by back titration of the excess acid. Evaporation of the dioxane solution at room temperature gave a thick, pale yellow oil which, after several extractions with dry ether, permitted the weighing of the residue of unchanged hexamethylenetetramine. Four experiments of this kind were run, all of which yielded amounts of ammonia corresponding to 95–97% of the calculated amount.

The combined ether extracts were dried with anhydrous sodium carbonate and evaporated, yielding a light yellow oil that could not be made to crystallize, and which decomposed on attempted distillation at 1 mm. pressure. This material was extremely soluble in all common solvents except cold 95% alcohol, and could not easily be purified. That it was triphenylmercaptomethylamine was indicated by its analysis, molecular weight and hydrolytic products.

Hydrolysis of Triphenylmercaptomethylamine.—Four and two hundred thirty-five thousandths grams of the condensation product from hexamethylenetetramine and

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(13) Bourgeois and Abraham, *Rec. trav. chim.*, **30**, 421 (1911).

(14) Mayer, *Ber.*, **42**, 3050 (1909).

(15) Fürth, *Monatsh.*, **27**, 844 (1906).

(16) A piece of litmus paper placed in the upper end of the condenser served to indicate when all of the ammonia had been driven over.

(17) Rieche, *Ber.*, **59**, 2181 (1926).

thiophenol was placed in a 125-cc. Erlenmeyer flask and dissolved in 30 cc. of glacial acetic acid. The solution was gently refluxed under a vertical condenser for two hours while dry hydrogen chloride was passed in through a capillary tube. The product was then transferred to a Claisen flask and the acetic acid distilled off at 25–35° (15–20 mm.) leaving a dark brown residue. This was repeatedly extracted with 10-cc. portions of boiling anhydrous ether and finally with small portions of boiling benzene until no more soluble material could be removed. The ether–benzene extract gave on evaporation 3.520 g. of a light yellow oil which crystallized on standing, and then melted at 36°, evidently formaldehyde-diphenylmercaptal. The dark brown residue in the flask was repeatedly extracted with hot water, giving a yellow solution which, after decolorizing with charcoal, gave on evaporation 0.610 g. of ammonium chloride. The latter was identified by the usual qualitative tests.

Assuming the original material to be $(C_6H_5SCH_2)_3N$, theory requires 3.830 g. of mercaptal and 0.590 g. of ammonium chloride as products of this conversion by dry hydrogen chloride. These figures check reasonably well with those obtained in the experiment.

Hydrobenzamide and Thiophenol.—From 5.96 g. of hydrobenzamide (0.02) mole and 3.34 g. of thiophenol (0.03 mole) refluxed for ten hours in 30 cc. of 1,4-dioxane, 0.178 g. of ammonia was evolved, as determined by back titration of excess standard acid with sodium hydroxide. Calcd., 0.170 g. The reaction product, isolated by evaporation of the dioxane solution at room temperature, was a crystalline mass weighing 9 g. This was twice recrystallized from 95% alcohol giving a colorless, odorless product melting at 79.5°, presumably benzalphenylmercaptobenzylamine.

Various other runs of this condensation gave amounts of ammonia corresponding to 97–104% of the theoretical.

Hydrolysis of Benzalphenylmercaptobenzylamine.—0.303 g. (0.001 mole) of the crystalline product from the condensation of hydrobenzamide and thiophenol was placed in a 50-cc. distilling flask and the side-neck of the latter connected to a vertical descending spiral condenser. Ten cc. of approximately 1 normal sulfuric acid was added and the mixture gently boiled for fifteen minutes, at the end of which about half the liquid had distilled over. To the milky liquid in the receiver was added 50 cc. of 95% alcohol, rinsed down through the condenser; 0.19 g. of lead acetate dissolved in 20 cc. of water was then added and the yellow precipitate which formed was stirred to promote crystallization. After a few minutes it was filtered off, washed with a small quantity of 50% aqueous alcohol, and dried at 100°.

The clear filtrate, which gave a negative test for thiophenol, was then treated with a solution of 0.22 g. of pure colorless phenylhydrazine in 20 cc. of 10% acetic acid. The white precipitate of the phenylhydrazone was stirred for a few minutes and then filtered off. It was washed once on the filter with 20% aqueous alcohol and then dried in the oven at 100°.

In this way, 0.210 g. of lead phenyl mercaptide was obtained, its identity being established by analysis (see below); calcd., 0.212 g. The weight of benzaldehyde phenylhydrazone (m. p. 156°) obtained was 0.360 g., whereas theory requires 0.392 g. However, the solubility of the hydrazone in cold dilute alcohol easily explains this discrepancy.

Analysis of Lead Phenyl Mercaptide.—0.205 g. of the mercaptide obtained above was slowly heated in a porcelain crucible until no more diphenyl sulfide was given off. At constant weight, 0.115 g. of lead sulfide remained, equivalent to 48.54% Pb. Calcd. for $Pb(SC_6H_5)_2$: Pb, 48.71.

Condensations of Other Hydramides and Mercaptans.—Numerous other condensations were carried out in the manner just described. In Table I are collected physical and analytical data concerning all of the reaction products thus far obtained.

TABLE I

PRODUCTS FROM THE CONDENSATION OF HYDRAMIDES WITH THIOPHENOLS OR MERCAPTANS

Hydramide	Product, amine	Crystal form, C = colorless	M. p., °C.
Hexamine[a]	Tri-phenylmercaptomethyl-	...	Oil
Hexamine	Tri-*p*-bromophenylmercaptomethyl-	C. glittering prisms[c]	135
Hexamine	Tri-*p*-nitrophenylmercaptomethyl-	Yellow needles[e]	146
Hexamine	Tri-*p*-cresylmercaptomethyl-	C. glittering prisms[g]	52
Hexamine	Tri-benzylmercaptomethyl-	C. needles[h]	46
Hydrobenzamide	Benzal-phenyl-mercaptobenzyl-	C. prisms[h]	79.5
Hydrobenzamide	Benzal-*p*-cresylmercaptobenzyl-	C. needles[h]	74
Hydrobenzamide	Benzal-benzylmercaptobenzyl-	C. needles[h]	67
3,3′,3″-Trinitrohydrobenzamide	3-Nitrobenzalphenylmercapto-3′-nitrobenzyl-	Pale yellow needles[h]	122
Hydro-*p*-toluamide	Methylbenzalphenylmercaptotolyl-	C. microcryst. powder[h]	71
Hydrofurfuramide	Furfural-phenylmercaptofurfuryl-	Small glittering prisms[k]	49

Formula	Molecular weight		Analyses, %					
	Calcd.	Found	Calcd.		Found			
$C_{21}H_{21}NS_3$	383	358, 369[b]	C, 65.79	H, 5.47	65.15	65.13	5.40	5.47
			N, 3.65	S, 25.09	4.16	4.28	25.73	
$C_{21}H_{18}NBr_3S_3$	620	597[d]	Br, 38.70		39.03			
$C_{21}H_{18}O_6N_4S_3$	528	520, 569[f]	S, 18.18		18.08			
$C_{24}H_{27}NS_3$	425		C, 67.76	H, 6.35	67.79	67.77	5.91	6.06
$C_{24}H_{27}NS_3$	425	417[b]	C, 67.76	H, 6.35	67.57	67.88	6.04	6.11
			N, 3.30	S, 22.60	3.52	3.60	22.30	
$C_{20}H_{17}NS$	303	285[b]	C, 79.16	H, 5.65	79.41	79.42	5.91	5.25
			N, 4.62	S, 10.57	5.05		9.98	
$C_{21}H_{19}NS$	317	303[d]	C, 79.49	H, 5.99	79.44		5.58	
			N, 4.41		4.72			
$C_{21}H_{19}NS$	317	293, 309[b]	C, 79.49	H, 5.99	78.60[j]		5.77	
$C_{20}H_{15}O_4N_3S$	393	401[d]	C, 61.07	H, 3.81	61.06		4.03	
$C_{22}H_{21}NS$	331		C, 79.75	H, 6.34	79.69		5.90	
$C_{16}H_{13}O_2NS$	283		C, 67.84	H, 4.55	67.88		4.63	

[a] Hexamethylenetetramine. [b] In freezing benzene. [c] From benzene. [d] In boiling, 1,4-dioxane. [e] From acetic acid. [f] In boiling benzene. [g] From 1:1 alcohol–ether. [h] From alcohol. [j] This compound burned only with great difficulty. [k] From ligroin (b. p. 70°); slowly turns brown on standing.

Summary

1. It has been shown that hexamethylenetetramine is decomposed by thiophenol when boiled with it in 1,4-dioxane solution. Two atoms of nitrogen per molecule of hexamethylenetetramine are eliminated as ammonia, the other product being $N(CH_2SC_6H_5)_3$.

2. Numerous other thiophenols and mercaptans have been shown to cause analogous decompositions of hexamethylenetetramine.

3. It has been shown that hydrobenzamide, hydrofurfuramide and other hydramides are partially decomposed by thiophenols when boiled in 1,4-dioxane solution. These reactions are of the same type, yielding the typical product RCH=NCH(SR′)R, as well as ammonia.

4. Evidence for the stoichiometry of these reactions has been presented, as well as data concerning products from eleven of them.

PRINCETON, NEW JERSEY

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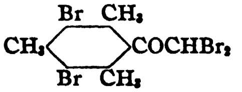
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Polyhalo Derivatives of Acetomesitylene. II. The Bromination of 3,5-Dichloroacetylmesitylene

BY C. HAROLD FISHER

In a former paper[1] it was reported that an excess of bromine reacted with 3,5-dibromoacetylmesitylene in acetic acid to give a sharply melting product which consists of equimolar quantities of α,α,3,5-tetrabromoacetylmesitylene (I) and α,α,α,3,5-pentabromoacetylmesitylene (II). Compound formation between di- and tribromomethyl phenyl ketones had not been described previously, and the introduction of three bromine atoms into the acetyl group is of interest in the light of the difficulty experienced[2] earlier in attempts to prepare tribromomethyl ketones[3] from acetophenones. To see if similar results could be obtained with other and simpler acetophenones, the bromination of 4-chloroacetophenone has been studied under similar conditions. It was found that only α,α-dibromo-4-chloroacetophenone was formed when an excess of bromine was used, either in acetic acid or in the absence of solvent. In view of the known ease of reduction of α-bromo ketones it seemed likely that the failure to obtain the tribromo ketone in this and other cases is due to the reducing action of the hydrogen bromide simultaneously formed. In this connection the action of hydrobromic acid on a hot acetic acid solution of pentabromoacetylmesitylene (II) was studied, and it was found that reduction to the tetrabromo ketone (I) occurred with ease.



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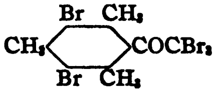

II

Attention was directed next to the bromination of an acetophenone, 3,5-dichloroacetylmesitylene (IV), more closely related to 3,5-dibromoacetylmesitylene.[1] The desired dichloro ketone (IV) was synthesized by the reduction with zinc and acetic acid of α,α,3,5-tetrachloroacetylmesitylene (III), which had been prepared by the chlorination of an acetic acid solution of acetomesitylene. That the tetrachloro ketone possesses the structure (III) assigned to it seems probable in view of the fact that sodium hypochlorite converted it, as well as 3,5-dichloroacetylmesitylene (IV), into α,α,α,3,5-pentachloroacetylmesitylene (V).

The bromination of 3,5-dichloroacetylmesitylene (IV) in acetic acid was found to be similar to the bromination of the corresponding dibromo

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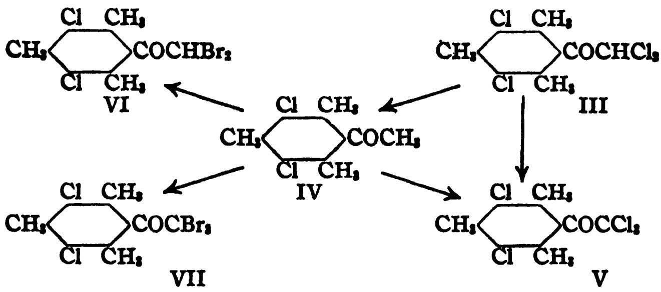
(1) Fisher, THIS JOURNAL, 55, 4241 (1933).

(2) Hunnius, *Ber.*, 10, 2010 (1877); Engler and Zielke, *ibid.*, 22, 204 (1889); Gabriel and Michael, *ibid.*, 11, 1007 (1878).

(3) It has been shown [Fuson and students, THIS JOURNAL, 54, 1114, 4380 (1932); other references may be obtained from these two papers] that hindered acetophenones may be converted into tribromomethyl ketones in good yield by treatment with sodium hypobromite.



ketone.[1] A sharply melting (103.5–104.5°) product was formed which was subsequently shown to be composed of α,α,α-tribromo-3,5-dichloroacetylmesitylene (VII) and α,α-dibromo-3,5-dichloroacetylmesitylene (VI). This product (m. p. 103.5–104.5°) was prepared also by crystallizing together equimolar quantities of its components (VI and VII); the separation of these components, however, could not be effected by repeated crystallization. As was expected, the action of sodium hypobromite caused conversion of the acetic acid bromination product (m. p. 103.5–104.5°) into the tribromo ketone (VII). The tribromo ketone (VII) was prepared also by the action of the same brominating agent on dichloroacetylmesitylene (IV). The dichlorodibromo ketone (VI) mentioned above was obtained by treating an acetic acid solution of 3,5-dichloroacetylmesitylene (IV) with two moles of bromine.

Experimental

α,α-Dibromo-4-chloroacetophenone.[4]—Attempts to prepare the tribromomethyl ketone were made unsuccessfully following the procedure (excess bromine, acetic acid solvent at 90–95°, stream of air to remove hydrogen bromide) outlined previously.[1] The tribromo compound was not isolated where the bromination was carried out without solvent, or in a carbon tetrachloride suspension of calcium carbonate. In each case the product obtained was the dibromomethyl ketone, m. p. 93.5–94.5° (previously given, 92.5°).[4]

Anal. Calcd. for $C_8H_5OClBr_2$: C, 30.7; H, 1.6. Found: C, 30.5; H, 1.8.

α,α,3,5-Tetrabromoacetylmesitylene (I).—A mixture of 1 g. of α,α,α,3,5-pentabromoacetylmesitylene, 10 cc. of 48% hydrobromic acid and 30 cc. of acetic acid was boiled for a few minutes and allowed to cool. The solid which appeared was collected, crystallized several times from alcohol and found to be tetrabromoacetylmesitylene.

α,α,3,5-Tetrachloroacetylmesitylene (III).—A stream of chlorine was bubbled, with mechanical stirring, into 8.1 g. of acetomesitylene and 10 cc. of acetic acid in a three-necked flask (to which a small amount of iodine and iron filings had been added) for one and one-half hours (8 g. of the gas was absorbed). Heat was generated and the product precipitated as a light-yellow paste. Crystallization from alcohol gave, in good yield, colorless needles melting at 106.5–107.5°.

Anal. Calcd. for $C_{11}H_{10}OCl_4$: C, 44.0; H, 3.4. Found: C, 44.1; H, 3.7.

3,5-Dichloroacetylmesitylene (IV).—A mixture of 6.7 g. of crude (the reaction product described above after removal of solvent) tetrachloroacetylmesitylene, 15 g.

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(4) Collet, *Bull. soc. chim.*, [3] 21, 70 (1899).

of zinc dust and 75 cc. of acetic acid was heated for three hours under a return condenser with a boiling water-bath. The mixture was filtered hot, and the residue washed with hot acetic acid. The combined filtrates were concentrated, and added to water. The solid which was precipitated crystallized from alcohol as large, colorless leaflets melting at 107.5–109°.

Anal. Calcd. for $C_{11}H_{12}OCl_2$: C, 57.1; H, 5.2. Found: C, 56.7; H, 5.4.

α,α,α,3,5-Pentachloroacetylmesitylene (V).—A solution of 0.5 g. of α,α,3,5-tetrachloroacetylmesitylene in 10 cc. of pyridine was added to 100 cc. of sodium hypochlorite (4 g. of sodium hydroxide in 40 cc. of water added to a chlorine-saturated solution of 6 g. of sodium hydroxide in 60 cc. of water), and the resulting mixture was mechanically agitated for forty-eight hours. The reaction product was filtered, washed with water and crystallized from alcohol. The colorless leaflets obtained melted at 90–91°, and was identical with the pentachloroacetylmesitylene prepared from 3,5-dichloroacetylmesitylene by treatment with sodium hypochlorite.

α,α,α,3,5-Pentachloroacetylmesitylene (V). (Second Method).—A solution of 2.3 g. of 3,5-dichloroacetylmesitylene in 20 cc. of pyridine was added to 280 cc. of sodium hypochlorite (80 cc. of 10% sodium hydroxide added to 200 cc. of chlorine-saturated 10% sodium hydroxide), and the resulting mixture agitated for sixty-nine hours. The residue obtained by filtering was washed with water and extracted with hot alcohol. The product was crystallized from alcohol, appearing as small leaflets (sometimes as needles) and melting at 90–91°.

Anal. Calcd. for $C_{11}H_9OCl_5$: C, 39.5; H, 2.7. Found: C, 39.4; H, 2.9.

Action of Bromine in Acetic Acid on 3,5-Dichloroacetylmesitylene.—Bromine (5 g.) was added from a dropping funnel, with mechanical stirring, to a solution of 1 g. of 3,5-dichloroacetylmesitylene in 15 cc. of glacial acetic acid contained in a three-necked flask surrounded by a water-bath. The dropping funnel was replaced by a tube extending beneath the surface of the solution and air was drawn through the solution (with heating and stirring) by a water-pump attached to condenser for one hour. Most of the excess bromine was then removed by an air-stream after stopping the flow of water in the condenser. The needles which appeared on cooling were crystallized from alcohol; m. p. 103.5–104.5°.

Anal. Calcd. for $C_{11}H_{10}OCl_2Br_2 \cdot C_{11}H_9OCl_2Br_3$: C, 30.8; H, 2.2. Found: C, 30.9; H, 2.4.

Crystallization of a Mixture of α,α-Dibromo-3,5-dichloroacetylmesitylene (VI) and α,α,α-Tribromo-3,5-dichloroacetylmesitylene (VII).—Crystallization of 0.39 g. of the dibromo ketone and 0.47 g. of the tribromo ketone gave 0.62 g. of colorless needles melting at 103–104°. The melting point was the same after six more crystallizations from alcohol, and it was not lowered by being mixed with the product obtained by the action of bromine (excess) in acetic acid on 3,5-dichloroacetylmesitylene.

α,α,α-Tribromo-3,5-dichloroacetylmesitylene (VII).—A solution of 3.5 g. of 3,5-dichloroacetylmesitylene in 20 cc. of pyridine was added to sodium hypobromite (9.5 cc. of bromine, 30 g. of sodium hydroxide and 280 cc. of water), and the resulting mixture agitated for forty-five hours. The solid obtained by filtration was washed with water and crystallized from alcohol. Stout needles (3.8 g.) melting at 84–85° were obtained.

Anal. Calcd. for $C_{11}H_9OCl_2Br_3$: C, 28.2; H, 1.9. Found: C, 28.3; H, 2.2.

The same tribromo ketone (VII) was obtained when 0.2 g. (in 2 cc. of pyridine) of the product (m. p. 103.5-104.5°) formed by the action of an excess of bromine in acetic acid on 3,5-dichloroacetylmesitylene was treated in a similar manner with sodium hypobromite (2 cc. of bromine, 6 g. of sodium hydroxide and 55 cc. of water).

α,α-Dibromo-3,5-dichloroacetylmesitylene (VI).—Bromine (6.4 g., 0.04 mole) was added, with stirring, from a dropping funnel during five minutes to 4.6 g. (0.02 mole) of 3,5-dibromoacetylmesitylene and 60 cc. of acetic acid in a three-necked flask surrounded by a water-bath. After one hour of stirring and heating, the solution was allowed to cool.

The crystalline material which appeared melted (after several crystallizations from alcohol) at 121–122°, and amounted to 5.7 g.

Anal. Calcd. for $C_{11}H_{10}OCl_2Br_2$: C, 33.9; H, 2.6. Found: C, 33.9; H, 2.7.

Summary

A satisfactory synthesis of 3,5-dichloroacetylmesitylene has been developed. It was found that the bromination of this acetophenone in acetic acid proceeded as in the case of 3,5-dibromoacetylmesitylene, giving a sharply melting product composed of the corresponding di- and tribromomethyl ketones. When 4-chloroacetophenone was brominated under the same conditions only α,α-dibromo-4-chloroacetophenone was isolated.

CAMBRIDGE, MASSACHUSETTS

RECEIVED JUNE 29, 1933
PUBLISHED NOVEMBER 7, 1933

[A COMMUNICATION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Michael Condensation. I. The Behavior of Diethyl Phenylmalonate in the Michael Condensation

BY RALPH CONNOR

The investigation of the reaction of diethyl phenylmalonate in the Michael condensation was undertaken for the purpose of studying the rearrangement which has been reported[1] in the reaction of diethyl methylmalonate, ethyl α-cyanopropionate and ethyl α-cyanobutyrate with α,β-unsaturated esters and ketones. This compound was selected because the tendency of an aryl group to migrate (according to the mechanism of Michael and Ross[1a,d]) or its influence upon the change in position of a carboethoxyl group (by the mechanism of Holden and Lapworth[1b]) might differ considerably from that of an alkyl group.

The first reaction carried out was that of diethyl phenylmalonate with ethyl crotonate in absolute alcohol containing a molecular equivalent of sodium ethoxide. Instead of the expected tribasic ester the products were diethyl carbonate and diethyl α-phenyl-β-methylglutarate (I). Similar results were obtained with ethyl tiglate, ethyl cinnamate and benzalacetophenone. It was also found that diethyl phenylmalonate in absolute alcohol with sodium ethoxide underwent alcoholysis to give diethyl carbonate and ethyl phenylacetate. This is analogous to the results obtained by Cope and McElvain[2] working with disubstituted malonic esters. Thus it appears that in the above reactions the phenylmalonic ester first underwent alcoholysis to give phenylacetic ester, which then added to the unsaturated esters and ketone.

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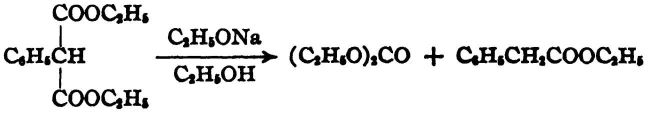
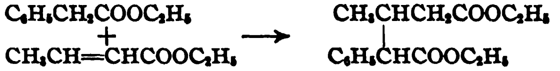
[1] (a) Michael and Ross, THIS JOURNAL, 52, 4598 (1930); 53, 1150 (1931). (b) Holden and Lapworth, *J. Chem. Soc.*, 2368 (1931). (c) Michael and Ross, THIS JOURNAL, 54, 407 (1932). (d) Michael and Ross, *ibid.*, 55, 1632 (1933).

[2] Cope and McElvain, *ibid.*, 54, 4319 (1932).



$$C_6H_5\underset{\begin{array}{c}|\\COOC_2H_5\end{array}}{\overset{\begin{array}{c}COOC_2H_5\\|\end{array}}{C}}H \xrightarrow[C_2H_5OH]{C_2H_5ONa} (C_2H_5O)_2CO + C_6H_5CH_2COOC_2H_5$$

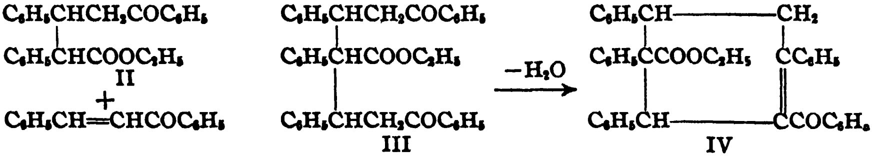


$$\begin{array}{c}C_6H_5CH_2COOC_2H_5\\+\\CH_3CH{=}CHCOOC_2H_5\end{array} \longrightarrow \begin{array}{c}CH_3CHCH_2COOC_2H_5\\|\\C_6H_5CHCOOC_2H_5\end{array}$$

I

In the hope that condensation of the diethyl phenylmalonate might be accomplished under conditions such that alcoholysis could not occur, the reaction was carried out in other media. The catalysts employed were (a) one-sixth of a molecular equivalent of sodium ethoxide in ether and (b) in benzene, (c) one equivalent of sodium ethoxide in ether, (d) piperidine with no solvent other than the ester and (e) diethyl sodiophenylmalonate in benzene. In the runs in which alcohol had been used to dissolve the sodium there was isolated a small yield of product corresponding to the addition of ethyl phenylacetate to the unsaturated ester or ketone. The only other condensation product obtained was from the runs in which benzalacetophenone was used under conditions (b) and (e) above. In the latter case (e) there was isolated a 9% yield of a condensation product melting at 258°. A trace of the same compound was obtained in the other reaction (b).

The same high melting product was formed by the reaction of ethyl α,β-diphenyl-γ-benzoylbutyrate (II) with benzalacetophenone in the presence of sodium ethoxide. The product of this reaction might be either of two normal addition products or the cyclic compounds derived from them.[3]



$$\begin{array}{c}C_6H_5CHCH_2COC_6H_5\\|\\C_6H_5CHCOOC_2H_5\\ \text{II}\\+\\C_6H_5CH{=}CHCOC_6H_5\end{array} \qquad \begin{array}{c}C_6H_5CHCH_2COC_6H_5\\|\\C_6H_5CHCOOC_2H_5\\|\\C_6H_5CHCH_2COC_6H_5\\ \text{III}\end{array} \xrightarrow{-H_2O} \begin{array}{ccc}C_6H_5CH & — & CH_2\\|&&|\\C_6H_5CCOOC_2H_5 && CC_6H_5\\|&&\|\\C_6H_5CH & — & CCOC_6H_5\\&\text{IV}&\end{array}$$

The analysis of the product indicated that it was probably the cyclohexene (IV), although the carbon and hydrogen percentages of the cyclohexene and cyclohexanone are so close that analysis is not conclusive. However, the structure IV is confirmed by the fact that the compound does not undergo alcoholysis when treated with sodium ethoxide in alcohol. Michael and Ross[1d] have found that the cyclohexanone formed by the reaction of two moles of benzalacetophenone with one of malonic ester readily undergoes alcoholysis. The unknown did not form a pyryllium

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(3) The normal condensation products, 2,3,4-triphenyl-3-carbethoxyl-1,5-dibenzoylpentane and ethyl α,β,δ-triphenyl-γ,ε-dibenzoylcaproate may lose a molecule of water or alcohol, respectively, to give a cyclohexene or cyclohexanone derivative.[1d]

salt with ferric chloride in acetic anhydride.[4] Saponification gave α,β-diphenyl-γ-benzoylbutyric acid.[5] In view of these reactions the unknown has been assigned the structure IV.[6]

The Michael condensation has been considered a typical reaction of the active methylene group[7] and is known to take place readily with malonic ester[1] and phenylacetic ester.[8] On first thought, therefore, it was surprising that diethyl phenylmalonate, which contains an additional labilizing group, should fail to undergo the reaction. The explanation for this behavior may lie in the fact that the additional group causes enough steric hindrance to render the phenylmalonic ester unreactive. This is in agreement with the report[1a] that diethyl ethylmalonate gives a smaller yield of condensation product with crotonic ester than does diethyl methylmalonate.

The fact that substitution plays an important role in determining the reactivity of a compound in the Michael condensation has been confirmed by a study of the reaction with structures which contain only one labilizing group—*i. e.*, the simple ketones and esters. With these compounds the major difficulty encountered has been that they are so reactive that it is difficult to prevent the formation of products arising from the combination of two moles of α,β-unsaturated compound with one of the ketones[9] or esters. This phase of the reaction is now under further investigation.

Experimental

Preparation of Reagents.—Ethyl crotonate, b. p. 136–139°, and ethyl tiglate, b. p. 152–154°, were prepared by the hydrogenation of ethyl acetoacetate and ethyl α-methylacetoacetate[10] and dehydration of the β-hydroxy esters with phosphorus pentoxide.[11]

TABLE I

THE RESULTS OF THE REACTION OF DIETHYL PHENYLMALONATE WITH α,β-UNSATURATED COMPOUNDS IN ALCOHOL[a]

Reactant	Yield, %		
	$(C_2H_5O)CO$ 124–126°	$C_6H_5CH_2CO_2C_2H_5$ 119–122° (23 mm.)	Condensation product
$CH_3CH{=}CHCOOC_2H_5$	46[f]	..	80[b]
$CH_3CH{=}C(CH_3)COOC_2H_5$	50	20	70[c]
$C_6H_5CH{=}CHCOOC_2H_5$	..	62	35[d]
$C_6H_5CH{=}CHCOC_6H_5$	..	..	94[e]
None	61	86	

[a] The reactions in alcohol were carried out according to the following general

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(4) Allen and Barker, THIS JOURNAL, 54, 743 (1932).

(5) The loss of benzalacetophenone during hydrolysis is an example of the reversal of the Michael condensation [*cf.* Ingold and Powell, *J. Chem. Soc.*, 119, 1976 (1921)]. Michael and Ross[1d] have found that the cyclohexene derivative obtained from the condensation of two moles of benzalacetophenone with one mole of malonic ester likewise loses benzalacetophenone during hydrolysis.

(6) The presence of the alcohol necessary to produce alcoholysis of the phenylmalonic ester to phenylacetic ester which then condensed to give IV may result from the action of sodium on phenylmalonic ester. It has been demonstrated that alcohol is formed by the action of sodium on esters [*cf.* Snell and McElvain, THIS JOURNAL, 53, 2310 (1931)].

(7) Ionescu, *Bull. soc. chim.*, [4] 51, 171 (1932).

(8) Borsche, *Ber.*, 42, 4497 (1909); Meerwein, *J. prakt. Chem.*, 97, 274 (1918).

(9) Kostanecki and Rossbach, *Ber.*, 29, 1493 (1896).

(10) Adkins, Connor and Cramer, THIS JOURNAL, 52, 5192 (1930).

(11) Courtot, *Bull. soc. chim.*, 35, 111 (1906).

method. To 4.6 g. (0.2 mole) of sodium in 70 cc. of absolute ethanol was added 47.2 g. (0.2 mole) of diethyl phenylmalonate[12] and 0.2 mole of the α,β-unsaturated compound. The solution was refluxed on the steam-bath for eight hours in the runs with ethyl cinnamate and benzalacetophenone and for twenty-four hours in the other runs. It was then cooled, poured into 500 g. of ice-water containing 13 g. of acetic acid, extracted with ether and dried over sodium sulfate. The runs with ethyl crotonate, ethyl tiglate and with no unsaturated compound present were distilled through a 15-cm. Widmer column. Ethyl α,β-diphenyl-γ-benzoylbutyrate was isolated by crystallization from the reaction mixture, washing with water containing acetic acid and drying. It gave the reported melting point (152–154°) after one recrystallization from ethanol. Unchanged esters were distilled from the ethyl α,β-diphenylglutarate and the residue recrystallized from ethanol.

[b] Diethyl α-phenyl-β-methylglutarate, b. p. 156–158° (6 mm.). *Anal.*[13] Calcd. for $C_{16}H_{22}O_4$: C, 69.06; H, 7.91. Found: C, 68.90; H, 7.86.

[c] Diethyl α-phenyl-β,γ-dimethylglutarate, b. p. 157.5–159.5° (5 mm.). *Anal.*[13] Calcd. for $C_{17}H_{24}O_4$: C, 69.86; H, 8.21; saponification equivalent, 146. Found: C, 69.94; H, 8.23; saponification equivalent, 143.

[d] Diethyl α,β-diphenylglutarate, m. p. 92–93°.[14]

[e] Ethyl α,β-diphenyl-γ-benzoylbutyrate, m. p. 152–154°.[15]

[f] Diethyl carbonate was identified by the formation of triphenylcarbinol, m. p. 161–162°, when it was allowed to react with phenylmagnesium bromide. The melting point was unchanged when mixed with an authentic specimen of triphenylcarbinol.

TABLE II

THE BEHAVIOR OF DIETHYL PHENYLMALONATE IN MEDIA OTHER THAN ALCOHOL[a]

Reactant[b]	Solvent	Yield, % Unreacted materials[c]	Compound II	Compound IV[m]
$C_6H_5CH{=}CHCOC_6H_5$[d]	....	97	0	0
$C_6H_5CH{=}CHCOC_6H_5$[e]	C_6H_6	84	9[f]	trace
$C_6H_5CH{=}CHCOC_6H_5$[g]	$(C_2H_5)_2O$	92	0	0
$C_6H_5CH{=}CHCOC_6H_5$[h]	$(C_2H_5)_2O$	85	5[f]	0
$C_6H_5CH{=}CHCOC_6H_5$[i]	C_6H_6	43[j]	0	9
$C_6H_5CH{=}CHCOOC_2H_5$[k]	C_6H_6	90	8[l]	0

[a] Benzoylacetic ester would be one of the products of condensation, rearrangement by the mechanism of Holden and Lapworth, and retrogression. In every distillate a test was made for benzoylacetic ester, using ferric chloride. There was never any color to indicate the presence of an enol.

[b] One-tenth mole of each of the reactants was used.

[c] Determined by distillation.

[d] This run was made with piperidine as a catalyst by the method of Kohler.[16]

[e] One-sixth of an equivalent of sodium was dissolved in 5 cc. of absolute alcohol, the reactants added and the mixture heated on the steam-bath with stirring for eight hours. Two-tenths gram of IV was filtered out and the filtrate treated in the usual manner.

[f] Ethyl α,β-diphenyl-γ-benzoylbutyrate, m. p. 152–154°.[15]

[g] The procedure of Michael and Ross[17] for the use of one-sixth of an equivalent of sodium ethoxide in ether was followed.

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(12) The author is indebted to Dr. V. H. Wallingford of the Mallinckrodt Chemical Works for a generous supply of diethyl phenylmalonate.

(13) These analyses were made by Mr. Ralph H. Wardlow.

(14) Avery and Maclay, THIS JOURNAL, 51, 2833 (1929).

(15) Avery and Jorgensen, *ibid.*, 52, 3628 (1930).

(16) Kohler, *Am. Chem. J.*, 46, 482 (1911).

(17) Michael and Ross, THIS JOURNAL, 52, 4605 (1930).

Carried out in the presence of one equivalent of sodium ethoxide.[17]

Diethyl sodiophenylmalonate was prepared from powdered sodium and diethyl phenylmalonate in 100 cc. of dry thiophene-free benzene, benzalacetophenone in 50 cc. of benzene added and the mixture refluxed gently with stirring for eight hours. A small amount of IV was filtered from the solution and the remainder of IV was obtained by washing the reaction mixture with aqueous acetic acid and concentrating the benzene layer. The solid was purified by suspension in hot ethanol and thorough washing with ether. It melted at 258° on the melting point bar[18] alone or mixed with the condensation product obtained by the reaction of ethyl α,β-diphenyl-γ-benzoylbutyrate with benzalacetophenone. Two grams was saponified with alcoholic potassium hydroxide. Acidification precipitated the solid acid, which after repeated recrystallization from benzene gave the lower melting isomer of α,β-diphenyl-γ-benzoylbutyric acid, m. p. 186.5–187.5°. The melting point was unchanged when mixed with an authentic sample of this acid.[15]

[i] The distillation residue was a stiff tarry material, evidently polymerized chalcone. It could not be crystallized.

[k] Diethyl sodiophenylmalonate was prepared and the procedure used as described under (*i*).

[l] Diethyl α,β-diphenylglutarate, m. p. 92–93°.[14]

[m] Compound IV was also prepared by the following method. To a solution prepared by dissolving 0.3 g. (0.013 mole) of sodium in 5 cc. of absolute ethanol was added 50 cc. of dry thiophene-free benzene and 5 g. (0.013 mole) of ethyl α,β-diphenyl-γ-benzoylbutyrate (II), followed by a solution of 2.7 g. (0.013 mole) of benzalacetophenone in benzene. The mixture was refluxed for eight hours, poured into 50 cc. of water containing 1 g. of acetic acid, the benzene layer separated and the solvent removed by distillation. The solid remaining was purified by suspending it in hot benzene, filtering and washing with ether. The material obtained melted at 258° on the melting point bar. The yield of pure material was 2.8 g. (38%). *Anal.*[13] Calcd. for $C_{40}H_{34}O_3$: C, 85.40; H, 6.04. Calcd. for $C_{38}H_{30}O_3$: C, 85.39; H, 5.62. Found: C, 85.15; H, 5.95.

An attempt to prepare a pyryllium salt[4] from 0.5 g. of this compound gave only unchanged material (m. p. 258°).

The conditions for alcoholysis used by Michael and Ross[19] for 1,5-diphenyl-2,6-dibenzoyl-4-carbethoxycyclohexanone-3 gave only unchanged material, even after standing for twenty hours (five times the time required for 60% alcoholysis of their compound).

Summary

It has been found that diethyl phenylmalonate does not undergo the Michael condensation. In alcohol solution diethyl carbonate and ethyl phenylacetate were formed and the latter condensed with α,β-unsaturated esters or ketones. In other media the only product isolated was a small amount of a cyclohexene derivative (IV) formed in benzene by the condensation of ethyl phenylacetate with two moles of benzalacetophenone. Since the failure of diethyl phenylmalonate to react suggested that increased substitution influences the reactivity of compounds in this reaction, a study of the simple ketones and esters has been undertaken.

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(18) Dennis and Shelton, THIS JOURNAL, 52, 3128 (1930).

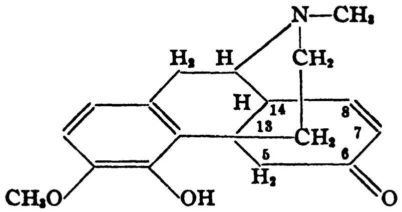
(19) Ref. 1d, p. 1624.

[CONTRIBUTION NO. 118 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

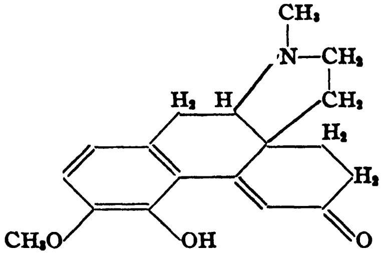
Metathebainone[1]

BY LYNDON F. SMALL AND ERICH MEITZNER

When thebaine is heated in concentrated hydrochloric acid with stannous chloride,[2] two phenolic ketones of the empirical composition $C_{18}H_{21}O_3N$ are formed. The structure of one of these, the "true" thebainone (Formula I)[3] is evident from the fact that it can be hydrogenated to the same dihydrothebainone as is obtained from the catalytic hydrogenation of thebaine.[4] The second of these phenolic ketones, metathebainone, for which Formula II has recently been proposed,[5] contains an alicyclic double bond which is indifferent to catalytic hydrogen[6] but is saturated by reduction with sodium amalgam in alkaline solution. The product, dihydrometathebainone (III),[7] is isomeric with the above-mentioned dihydrothebainone.



I. "True" Thebainone



II. Metathebainone

While the Schöpf metathebainone formula (II) offers the only satisfactory explanation of these facts, the point of attachment of the nitrogen-containing ring and the location of the double linkage rests almost entirely upon speculative evidence, namely, exclusion of other positions, and the extraordinary resemblance of metathebainone to α,β-unsaturated ketones of the type of salicylidene acetone.[5,8] The isolation from a reduction of metathebainone of a diastereomer of the known dihydrometathebainone would constitute a direct proof of the position of the metathebainone double linkage at C-5, C-13 (*i. e.*, at a carbon atom which becomes asym-

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(1) This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc., and the Rockefeller Foundation.

(2) Pschorr, Pfaff and Herrschmann, *Ber.*, **38**, 3160 (1905).

(3) Schöpf and Hirsch, *Ann.*, **489**, 224 (1931).

(4) Freund, Speyer and Guttmann, *Ber.*, **53**, 2250 (1920); Skita, Nord, Reichert and Stukart, *ibid.*, **54**, 1560 (1921).

(5) Schöpf and Borkowsky, *Ann.*, **458**, 148 (1927).

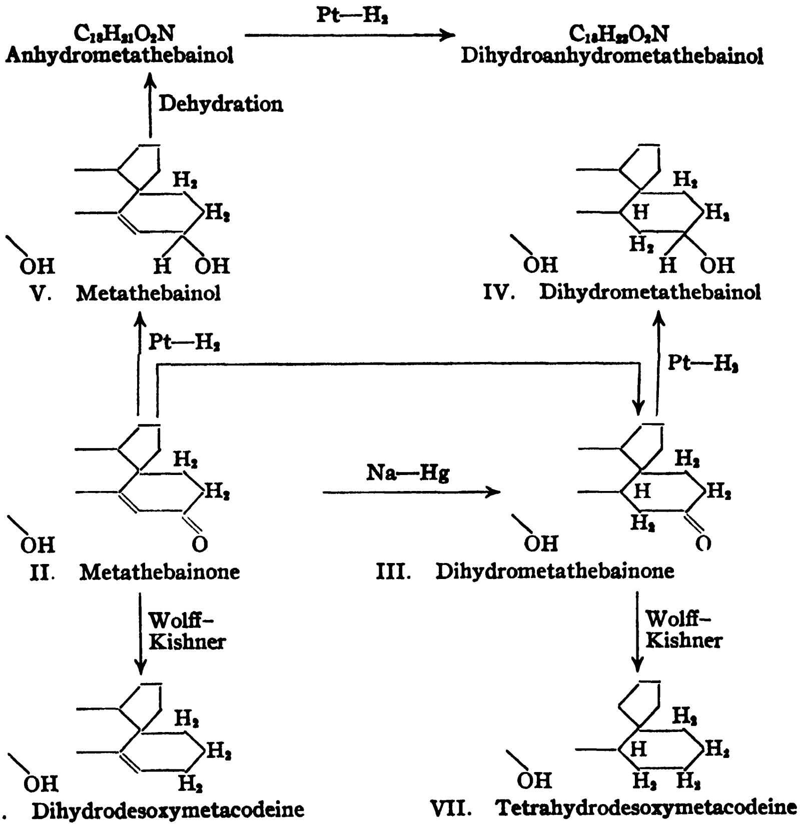
(6) Heinz Hoek, Dissertation, Munich, 1926.

(7) The thebainol of Pschorr,[2] who believed it to be a secondary alcohol; its ketone nature was demonstrated by Gulland and Robinson.[8] A recent review of the chemistry of metathebainone may be found in the "Chemistry of the Opium Alkaloids," by Small and Lutz, U. S. Government Printing Office, 1932, pp. 308–321.

(8) Gulland and Robinson, *J. Chem. Soc.*, **123**, 998 (1923).

metric on reduction),[9] and hence of the ethanamine side chain at C-14.[10] Such a diastereomer, designated as β-dihydrothebainone, from catalytic hydrogenation of metathebainone, was described by Kondo and Ochiai[11] without mention of its significance for the metathebainone formula. The present investigation was undertaken with a view to obtaining by reductive methods more definite evidence on the structure of metathebainone; while the desired proof of structure has not been obtained, nothing has been found which is not in accord with Schöpf's formula.

Metathebainol.—Under the conditions imposed by Hoek (base in alcohol or in excess of dilute acetic acid), metathebainone takes up no hydrogen



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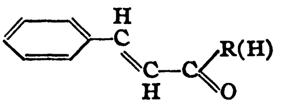
[9] The dihydro-epi-thebainone of Schöpf and Winterhalder [*Ann.*, 452, 239 (1927)], which must still contain the thebaine nitrogen ring system, is apparently the stereoisomer on C-14 [compare, however, Small and Cohen, This Journal, 53, 2237 (1931)] of dihydrothebainone, and is different from dihydrometathebainone; it may therefore be assumed that dihydrometathebainone does not represent one of the two diastereomers which might be derived from the saturation of a hypothetical double linkage at C-8, C-14. See Schöpf and Borkowsky, *Ann.*, 458, 155 (1927).

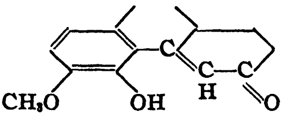
[10] Schöpf and Borkowsky, *ibid.*, 458, 159 (1927). The morphol degradation of methylmetathebainonemethine [Knorr and Pschorr, *Ber.*, 38, 3172 (1905)] makes attachment of the ethanamine chain at other than a tertiary carbon atom unlikely.

[11] Kondo and Ochiai, *J. Pharm. Soc. Japan*, No. 549, 913 (1927); *Ann.*, 470, 232 (1929).

with palladium or platinum. When hydrogenation is carried out under the conditions of Kondo (base neutralized with dilute hydrochloric acid), or as we later found, on an aqueous solution of the base, one mole of hydrogen is absorbed readily. The product is a mixture of two substances, as might be suspected from the constants given by Kondo for the supposed β-dihydrothebainone. The main product (65% or more) is not a dihydro ketone, but the isomeric α,β-unsaturated alcohol (V) which we have named metathebainol. It is obtained in quantitative yield when metathebainone is hydrogenated in the presence of platinum oxide at two to three atmospheres pressure. The second product isolated from hydrogenation at atmospheric pressure is a ketone, obtained in about 5% yield as the semicarbazone. This was dextrorotatory, and proved to be identical with the already-known semicarbazone of dihydrometathebainone (III).

While these findings invalidate any support which may have been lent to the C-5, C-13 location of the double linkage by the supposed existence of a second dihydrometathebainone, the formation of the same dihydro ketone as in the sodium amalgam reduction does not necessarily weigh against the Schöpf formula. It seems not improbable that the catalytic saturation of the double bond has been accomplished through the same mechanism which we believe functions in the sodium amalgam reduction, namely, a primary 1,4-addition of hydrogen.[12] Metathebainol, which does not present this opportunity for a 1,4-addition, is completely indifferent to sodium amalgam or catalytic hydrogen. The predominating 1,2-addition at the carbonyl group recalls the hydrogenation of α,β-unsaturated ketones and aldehydes containing a system not dissimilar to that of metathebainone





where it could be demonstrated, particularly in the case of cinnamic aldehyde, that the course of normal hydrogenation consisted of a primary reduction of the carbonyl oxygen to hydroxyl.[13]

Metathebainol does not give any of the characteristic reactions for the keto group. The presence of two hydroxyl groups is shown by the formation of a diacetyl derivative, which may be saponified to yield metathebainol and a small amount of a new base of unknown nature. The acetyl group on the phenolic hydroxyl of metathebainol, while stable toward alcoholic potassium acetate at 140°, is split off easily by an aqueous solu-

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(12) A prediction from Skita's rule [Skita, *Ann.*, 431, 1, 15 (1923); Skita and Faust, *Ber.*, 64, 2878 (1931)] that diastereomeric compounds should appear in the two types of reduction involved, does not seem warranted where the possibility of 1,4-addition is present.

(13) Straus and Grindel, *Ann.*, 439, 276 (1924); compare Tuley and Adams, THIS JOURNAL, 47, 3061 (1925).

tion of hydroxylamine hydrochloride at room temperature.[14] The resulting compound is phenolic and still contains one acetyl group; whether other changes in the molecule take place was not investigated. Monoacetylthebainol shows marked thermochromism;[15] the colorless solution in cold alcohol or bromobenzene gives a reversible change to pink on warming. The colored solution is apparently not affected by oxygen, and the monoacetyl compound can be recovered unchanged from the experiment.

Metathebainol shows no halochromism with cold hydrochloric acid, but is changed slowly to a substance which gives a highly-colored solution; the color disappears on dilution with water, and a new halogen-containing base can be isolated. The monoacetyl and diacetyl derivatives likewise show no immediate halochromism, but are converted to halochromic compounds on standing in acid solution.

Metathebainol crystallizes associated with one molecule of methanol or chloroform. While, as noted above, the alkaloid or its compound with methyl alcohol is indifferent to catalytic hydrogenation, the compound with chloroform was observed to absorb one molecule of hydrogen. The product was pure metathebainol hydrochloride. The hydrogen chloride was obviously derived from catalytic hydrogenation of the chloroform of crystallization, and experiments have shown us that chloroform, in the presence of such a saturated base as dihydrocodeine, can be hydrogenated with ease, one molecule of hydrogen being absorbed for each molecule of base present.[16]

Anhydrometathebainol.—When metathebainol is heated to 160° with alcoholic potassium hydroxide, it loses one molecule of water to give a new base, $C_{18}H_{21}O_2N$, which we shall designate as anhydrometathebainol. It must contain two alicyclic double bonds, one of which apparently still occupies the metathebainol C-5, C-13 position, for it is possible to effect addition of but one mole of hydrogen catalytically. The second double linkage might be expected at C-6, C-7; the hydrogenation product, dihydroanhydrometathebainol is, however, different from the dihydrodesoxymetacodeine (VI) to be described below. It is probable, therefore, that the formation of anhydrometathebainol has involved a deeper-seated structural change (perhaps to a morphothebaine type) than mere dehydration in ring III.

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(14) A similar saponification by cold hydroxylamine hydrochloride was observed by Pschorr[3] in the case of acetylmetathebainone.

(15) A recent account of thermochromic phenomena is given by Bergmann and Corte, *Ber.*, 66, 39 (1933). The hypothesis of Bergmann that the presence of a cross-conjugated system is necessary for thermochromism leads us to suspect that the saponification with hydroxylamine hydrochloride may have been accompanied by other structural changes.

(16) Catalytic hydrogenation of carbon tetrachloride, bromoform and iodoform in the presence of sodium ethylate has been described by Kelber, *Ber.*, 50, 305 (1917); Busch and Stöve, *ibid.*, 49, 1063 (1916). Borsche and Heimbürger, *ibid.*, 48, 850 (1915), cite the experiment of Ottmers, who could reduce the halogen out of isopinol dibromide only when the hydrogen bromide formed was taken care of by piperidine or quinoline.

Dihydrometathebainol.—The alicyclic double bond of metathebainol resists reduction, but the saturated alcohol, dihydrometathebainol, (IV) may be prepared indirectly from metathebainone through dihydrometathebainone (III). The last-named compound adds one molecule of hydrogen readily in the presence of platinum (oxide), yielding a secondary alcohol, which is isomeric with the two known epimeric dihydrothebainols derived from the dihydrothebainone series.[17] The isomerism might be due: (a) to a difference in the ring position (at C-6 or C-8) of the alcoholic hydroxyl (most improbable, because of the relationship of metathebainone to codeinone[18] (*cf.* also Schöpf[19]); (b) to a difference in the point of attachment of the ethanamine side chain (the question of the generation of a new asymmetric center at C-14 has already been considered[9]).

The Hydrodesoxymetacodeines.—We have attempted to eliminate consideration (a) of the preceding paragraph through the preparation of hydrogenated derivatives of a hypothetical desoxymetacodeine. When metathebainone is heated with hydrazine hydrate and sodium ethylate (method of Wolff–Kishner), reduction of the keto group takes place[20] and a good yield of a new base, $C_{18}H_{23}O_2N$, is obtained. Dihydrodesoxymetacodeine (VI) is isomeric with the dihydrodesoxycodeines derived from the normal codeine series.[21] Like its parent substance, metathebainone, it resists hydrogenation, but since the α,β-unsaturated ketone system postulated by the Schöpf formula has been destroyed, it shows no halochromism.

Under the same conditions of reduction, dihydrometathebainone is converted in about 80% yield to the corresponding saturated tetrahydrodesoxymetacodeine (VII). The new base is different from its well-known isomer tetrahydrodesoxycodeine,[22] and must owe its isomerism to a difference in point of attachment of the nitrogen-containing side chain.[23]

It is a pleasure to acknowledge here the generosity of Merck and Co , Rahway, N. J., in supplying the thebaine used in this research.

Experimental

Metathebainone.—This base was prepared according to the directions of Gulland and Robinson.[8] By this method, which involves a final neutralization with sodium bicarbonate, a yellow metathebainone, as the compound is described throughout the literature, was always obtained. The crystals were of a color close to that of picric acid, and retained this color unchanged through very numerous recrystallizations. When the final neutralization was carried to distinctly alkaline reaction with sodium hydroxide or ammonia, the crude metathebainone was only faintly yellow, and after several crystallizations from ethanol by addition of methanol was obtained as white crystals which showed no tinge of yellow when compared with pure anhydrous sodium sulfate. The white and yellow specimens have the same melting point. Both give yellow solutions in ethanol or water, colorless solutions in benzene or chloroform. For the yellow specimen, in benzene, $[\alpha]_D^{24}$ −419° (c = 1.966); for the white specimen, $[\alpha]_D^{25}$ −417° (c = 1.802).

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[17] Speyer and Siebert, *Ber.*, **54**, 1519 (1921); Kondo and Ochiai, *J. Pharm. Soc. Japan*, No. **538**, 99 (1926); *Ann.*, **470**, 224 (1929).

[18] Knorr, *Ber.*, **38**, 3171 (1905).

[19] Schöpf and Hirsch, *Ann.*, **489**, 229, Note 3 (1931).

[20] Clemmensen reduction of metathebainone or of dihydrometathebainone results in dark resinous products; our experiments in this line agree with those already reported by Hoek.

[21] Small and Cohen, THIS JOURNAL, **53**, 2227 (1931).

[22] Small and Cohen, *ibid.*, **54**, 802 (1932).

[23] The possibility that rearrangement may have taken place under the vigorous conditions imposed must be mentioned, since metathebainone and dihydrometathebainone heated with sodium ethylate alone at 180° were found to be altered. The products in this case, however, were disagreeable resins, and the good yield of clean crystalline products from the Wolff–Kishner conditions speaks for a rapid primary formation of the hydrazone and transformation of the latter to the completely alkali-stable desoxy product.

Metathebainol (V).—Ten grams of metathebainone was neutralized with 0.2 *N* hydrochloric acid and reduced in the presence of 0.15 g. of platinum oxide at 2 to 3 atmospheres gage pressure until no further absorption took place (three to twelve hours). After removal of catalyst the solution was made ammoniacal and the clear liquid extracted with 30 cc. of chloroform. From the chloroform 7 to 8 g. of the metathebainol–chloroform addition product crystallized after short standing. The mother liquor from this crystallization was combined with the chloroform from two more extractions, evaporated nearly to dryness, and taken up in a little methanol. Four to five grams more of a somewhat less pure product was thus obtained.

Metathebainol crystallizes from chloroform in white crystals which melt at 87–88° with loss of chloroform. In absolute alcohol $[\alpha]_D^{25}$ −45.3, −45.9° (c = 3.490, 2.525) was observed. The chloroform compound loses a portion of its chloroform on exposure to air and combustion analyses were not consistent; direct determination of chloroform was difficult on account of the ease with which the base distils.

Anal. Calcd. for $C_{18}H_{23}O_3N + CHCl_3$: $CHCl_3$, 28.4. Found: $CHCl_3$, 27.1, 30.2.

The solvent-free base could be obtained only as a faintly yellow resin ($[\alpha]_D^{25}$ −66.7° in absolute alcohol, c = 2.781) which gave with chloroform the crystalline addition compound again, or gave with methanol white crystals of m. p. 92–93°. These showed $[\alpha]_D$ −60.3, −61.2° (absolute alcohol, c = 2.134, 2.043; t = 24, 27°). The solvated crystals as brought to analysis always contained less than one molecule of methanol.

Anal. Calcd. for $C_{18}H_{23}O_3N + CH_3OH$: C, 68.43; H, 8.16; CH_3OH, 9.6. Calcd. for $C_{18}H_{23}O_3N + 0.8CH_3OH$: C, 69.04; H, 8.08; CH_3OH, 7.8. Found: C, 68.83; H, 8.13; CH_3OH, 7.6. Calcd. for $C_{18}H_{23}O_3N$: C, 71.71; H, 7.70. Found: (dried at 120°) C, 71.70; H, 8.03.

Metathebainol was regained unchanged from shaking in alkaline solution for seven hours with sodium amalgam; from boiling in alcohol solution with sodium amalgam, with occasional addition of glacial acetic acid; from treatment with sodium in alcohol; from shaking the chloroform-free base in alcohol with platinum oxide under hydrogen. When metathebainol containing crystal-chloroform was hydrogenated in alcohol with platinum oxide catalyst, one mole of hydrogen was absorbed. The product was isolated by evaporating the solution to a small volume and adding warm ethyl acetate. White crystals were obtained, which melted at 162° (gas evolution), resolidified and decomposed above 220°. The compound proved to be metathebainol hydrochloride containing one molecule of ethyl acetate.

Anal. Calcd. for $C_{21}H_{32}O_5NCl$: C, 60.92; H, 7.79. Found: C, 60.95; H, 7.57.

Metathebainol is exceedingly stable toward alkali. It was recovered unchanged after boiling with 25% potassium hydroxide for fifteen minutes, or from heating six hours with sodium ethylate solution at 125° (sodium ethylate or alcoholic potassium hydroxide at 160° effects dehydration, see anhydrometathebainol). Metathebainol in concentrated hydrochloric acid gives a colorless solution which slowly (rapidly at 60°) becomes green and finally a pure blue halochromic solution results. The blue color disappears with reducing agents, as zinc or stannous chloride, and if these are present at the beginning no color develops. Stannous chloride or salts of other heavy metals yield insoluble double salts. The base isolated from the halochromic solution was not crystalline; it contained halogen, and on catalytic hydrogenation took up one molecule of hydrogen to give the hydrochloride of a new (amorphous) base. Metathebainol gave no oxime or semicarbazone, but appeared to be decomposed by the reagents. With nitrous acid it gave an intense red color.

Metathebainol hydriodide was prepared in the usual way and purified from water.

Anal. Calcd. for $C_{18}H_{23}O_3N \cdot HI + H_2O$: I, 28.38. Found: I, 28.25, 28.11.

Metathebainol methiodide was prepared in the usual way and purified from alcohol; m. p. 225°.

Anal. Calcd. for $C_{19}H_{26}O_3NI$: I, 28.65. Found: I, 28.67.

Diacetylmetathebainol.—A solution of 1 g. of metathebainol in 4 cc. of acetic anhydride was allowed to stand for two hours at room temperature, poured into water, made ammoniacal, and the precipitate extracted with ether. The product obtained weighed 0.75 g. and after recrystallization from dilute methyl alcohol melted at 140°. It was non-phenolic; the solution in hydrochloric acid was colorless, but exhibited strong green-blue halochromism on standing. Diacetylmetathebainol in alcohol with platinum oxide could not be hydrogenated.

Anal. Calcd. for $C_{22}H_{27}O_5N$: C, 68.53; H, 7.06. Found: C, 68.78, 68.49; H, 7.29, 6.96. Calcd. for $C_{18}H_{21}O_3N(COCH_3)_2$: $COCH_3$, 22.4. Found: (Freudenberg) $COCH_3$, 22.1.

Diacetylmetathebainol was recovered unchanged after heating in absolute alcohol with potassium acetate for one hour at 130°. For saponification, 2.9 g. of diacetylmetathebainol was boiled for ten minutes with 20 cc. of 25% aqueous alcoholic potassium hydroxide. The solution was diluted, ammonium chloride added, and the precipitate extracted with chloroform. The residue from distillation of the chloroform was taken up in 20% acetic acid and a concd. solution of 2 g. of potassium iodide added. A crystalline hydriodide, 0.7 g., separated, from which small amounts of a new base of m. p. 150° were obtained. This gave a mixed melting point depression of 30° with monoacetylmetathebainol of the same melting point, and its nature is unknown. From the mother liquor of the hydriodide precipitation, 1 g. (= 32% of the calculated amount) of metathebainol-chloroform could be isolated.

Monoacetylmetathebainol.—A solution of 1 g. of diacetylmetathebainol and 0.4 g. of hydroxylamine hydrochloride in a little water was allowed to stand for one hour. Sodium carbonate was added and the precipitated base extracted into ether. On evaporation of the solvent and addition of warm ethyl acetate, white crystals were obtained which could be purified from ethyl acetate. The compound turns pink at about 143° and melts to a red liquid at 150°. A solution of acetylmetathebainol in alcohol or bromobenzene becomes pink on heating, and the color disappears on cooling; this may be repeated many times. No sensitiveness to oxygen was noted, and the compound was regained unchanged. Acetylmetathebainol has the properties of a phenol. It does not show immediate halochromism in concentrated hydrochloric acid, but is slowly changed by the acid so that a green-blue solution results. The base gave values for nitrogen which were consistently too high, and we do not consider the structure we have given it to be certain.

Anal. Calcd. for $C_{20}H_{25}O_4N$: C, 69.93; H, 7.34; N, 4.08. Found: C, 69.60, 69.76; H, 7.42, 7.39; N, 4.91, 4.78. Calcd. for $C_{18}H_{22}O_3N(COCH_3)$: $COCH_3$, 12.54. Found: (Freudenberg) 12.81.

Hydrogenation of Metathebainone. Method of Kondo and Ochiai.[11]—Two grams of metathebainone, neutralized with dilute hydrochloric acid, with 0.5 g. of charcoal (Eastman Kodak "Special") and 2 cc. of 1% palladous chloride solution absorbed 140 to 150 cc. of hydrogen (several experiments). The solution was made ammoniacal, the bases extracted into chloroform, and the extract concentrated to a small volume; on addition of methanol and cooling 1.5 to 1.6 g. (60–65%) of metathebainol-chloroform separated. The mother liquor (which contained more metathebainol) was treated with dilute acetic acid, and sodium acetate and semicarbazide hydrochloride added. After twelve hours sodium carbonate was added and the white precipitate extracted with chloroform. This yielded 0.1 g. (5% of the calculated amount) of a semicarbazone of m. p. 217–218° and $[\alpha]^{25}_{\mathrm{D}}$ +88.4° (10% acetic acid, c = 1.289). When mixed with dihydrometathebainone semicarbazone of m. p. 232° and $[\alpha]^{27}_{\mathrm{D}}$ +109.8°[24] it melted at 226°.

Dihydrometathebainol (IV) was obtained by hydrogenation (1 mole of hydrogen) of dihydrometathebainone in alcohol with platinum oxide. The free base, which formed poorly defined crystals of m. p. about 120°, gave a well-defined hydriodide having $[\alpha]^{30}_{\mathrm{D}}$ +16.4° (water, c = 4.128).

Anal. Calcd. for $C_{18}H_{26}O_3NI + 2H_2O$: C, 46.24; H, 6.47; I, 27.17; H_2O, 7.7. Found: C, 46.40; H, 6.14; I, 27.35; H_2O, 7.7.

Dihydrodesoxymetacodeine (VI).—A solution of 1.5 g. of metathebainone and 1 cc. of hydrazine hydrate in 15 cc. of absolute alcohol containing 0.7 g. of sodium was heated in a sealed tube to 180° for three hours. The nearly colorless solution was poured into water, ammonium chloride added, and the precipitated base extracted with ether. The residue from distillation of the ether yielded 0.8–0.9 g. (56–63% of the calculated amount) of crystals on treatment with a little methanol. As recrystallized from methanol the base sinters at 65°, melts at 72°, but soon becomes amorphous through loss of methanol. It distils readily at 130–135° at 0.001 mm., forming a colorless resin which becomes crystalline with methanol. Analysis and rotation were made on the distilled solvent-free product. In absolute alcohol, $[\alpha]^{24}_{\mathrm{D}}$ −93.8° (c = 1.109) was found.

Anal. Calcd. for $C_{18}H_{23}O_2N$: C, 75.74; H, 8.12. Found: C, 75.43; H, 7.95.

An alcoholic solution of dihydrodesoxymetacodeine absorbed no hydrogen (platinum oxide catalyst). The base gave no halochromism with concentrated hydrochloric acid, even on heating. In one attempted preparation of the desoxy compound, insufficient heating resulted in the formation of a bright yellow compound, sparingly soluble in alcohol or ether, m. p. 200–210° with decomposition, which was apparently the ketazine of metathebainone.

Tetrahydrodesoxymetacodeine (VII).—A solution of 1.8 g. of dihydrometathebainone (solvent-free) and 1 cc. of hydrazine hydrate in 15 cc. of absolute alcohol containing 0.9 g. of sodium was heated in a sealed tube at 170–180° for six hours. The light yellow liquid was diluted with water, the base precipitated with ammonium chloride and extracted into ether. The product was amorphous, but gave 2.1 g. of well crystallized hydriodide (80% yield). In aqueous solution the hydriodide showed $[\alpha]^{28}_{\mathrm{D}}$ −12.5° (c = 1.928).

Anal. Calcd. for $C_{18}H_{26}O_2NI$: C, 52.03; H, 6.31; I, 30.58. Found: C, 52.11; H, 6.55; I, 30.12.

Anhydrometathebainol.—Three grams of solvated metathebainol was freed from chloroform at 100° and 15 mm. pressure and dissolved in 20 cc. of 95% alcohol containing 0.7 g. of potassium hydroxide. After heating at 160° for one and one-half hours in a sealed tube the solution was poured into water, treated with ammonium chloride and extracted with ether. The brown residue from evaporation of the ether became crystalline with warm methanol; yield 1.2 to 1.3 g. (53–57%). The base melts at 106–107° with decomposition; it distils at 130° and 0.001 mm. as a colorless resin, which yields the crystals of m. p. 107° with methanol. The solvent-free base turns quite brown in twenty-four hours. It dissolves colorless in concentrated hydrochloric acid, then develops a green-blue halochromism. For the solvent-free base the specific rotation was $[\alpha]_D^{25}$ $-201°$ (absolute alcohol, $c = 1.813$).

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[24] From sodium amalgam reduction of metathebainone; Gulland and Robinson[8] give the melting point of the semicarbazone as 216–218°, specific rotation not given.

Anal. Calcd. for $C_{18}H_{21}O_2N$: C, 76.28; H, 7.47. Found: C, 76.15; H, 7.73.

Acetylanhydrometathebainol was prepared by the method used for diacetylmetathebainol. It was purified from methanol and melted at 166°. In alcohol with platinum oxide it absorbed one mole of hydrogen.

Anal. Calcd. for $C_{20}H_{23}O_3N$: C, 73.80; H, 7.13. Found: C, 73.35, 73.46; H, 7.23, 7.36.

Dihydroanhydrometathebainol was prepared by hydrogenation of anhydrometathebainol in alcohol with platinum oxide. It crystallizes from methanol in white crystals which are stable only while in contact with the solvent. It distils at 130° and 0.001 mm. as a colorless stable resin, which crystallizes in contact with methanol. In concentrated hydrochloric acid a green-blue halochromism slowly develops.

Anal. Calcd. for $C_{18}H_{23}O_2N$: C, 75.74; H, 8.12. Found: C, 75.63; H, 8.39.

Summary

1. Hydrogenation of metathebainone in aqueous solution or as the hydrochloride results in formation of a secondary alcohol, metathebainol, together with a small amount of dihydrometathebainone.

2. The so-called β-dihydrothebainone of Kondo is a mixture of metathebainol and dihydrometathebainone. The existence of a diastereomer of dihydrometathebainone, which could serve as proof of the Schöpf metathebainone formula, has not yet been demonstrated.

3. Catalytic hydrogenation of dihydrometathebainone leads to a saturated secondary alcohol, dihydrometathebainol.

4. Metathebainone and dihydrometathebainone can be reduced by the method of Wolff–Kishner to desoxy derivatives isomeric with the dihydrodesoxycodeines and tetrahydrodesoxycodeine, respectively.

5. Through dehydration of metathebainol an anhydrometathebainol of uncertain structure is obtained.

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Reactions of Aldoxime Derivatives with Bases. I. The Reactions of Certain Acetyl-β-aldoximes with Alkali[1]

BY CHARLES R. HAUSER AND C. T. SULLIVAN

It seems to be rather generally agreed that when the acetyl derivatives of two geometrically isomeric aldoximes react with alkali, the β-isomer forms the nitrile,[2] and the α-isomer, the original oxime. Recently, however, Brady and McHugh[3] have isolated the corresponding β-oxime in addition to the nitrile from the reaction products of certain acetyl aldoximes and 2 *N* sodium hydroxide. They state, "The isolation of the β-aldoxime by treating with cold sodium hydroxide suggested that the supposed acetyl derivatives were contaminated with unchanged oxime. . . . An alternative explanation is that the hydrolysis of the acetyl-β-oxime gave partly nitrile and partly β-oxime, . . . Judging from experience in the hydrolysis of other acyl-β-aldoximes, we think the second contingency the less likely."

In connection with a study of the mechanism of decomposition of acyl-β-aldoximes in the presence of bases, we have determined the products formed when certain acetyl-β-aldoximes react with alkali. It has been found that when certain acetyl-β-aldoximes were decomposed by sodium hydroxide at 30°, yields of more than 50% of nitriles and 25–30% of β-oximes were obtained. At 0°, on the other hand, the yields of nitriles were only about 30%, while those of the β-oximes were more than 50% of the theoretical quantities (Tables II and III). Experimental evidence has been obtained which indicates that the acetyl compounds used in this work were essentially pure substances. These results show that acetyl-β-aldoximes react with alkali to form partly nitrile and partly β-oxime. Thus both α- and β-acetyl aldoximes are hydrolyzed by alkali to form the corresponding oxime; the β derivatives, however, in addition to the hydrolysis, undergo simultaneous decomposition leading to the formation of nitriles. The latter reaction apparently has the higher temperature coefficient since at 30° it is the predominant reaction, whereas at 0° the hydrolysis predominates.

Experimental

Acetyl-β-aldoximes.—These substances were prepared by a modification of the method described by Brady and McHugh.[3] A solution of 4 g. of β-4-methoxybenzaldoxime in a minimum (about 4.5 cc.) of acetic anhydride was kept at room temperature for five minutes and then cooled in an ice-bath until a solid formed. The suspension was dissolved in alcohol, the solution filtered, and cold water added to the filtrate until the cloudiness first produced just disappeared on shaking. On cooling, crystals were obtained. If the product possessed the odor of anhydride it was recrystallized from a cold acetone–alcohol–water mixture as described above. An alternative procedure was to shake the anhydride suspension with ice water until the anhydride was decomposed.[4] The precipitate was then filtered off and recrystallized as above. The acetyl derivative was obtained as white needles, melting at 64–65°. (A mixed m. p. determination with β-oxime was 54–57°, and one with nitrile, below 50°.) This acetyl aldoxime was prepared also according to the procedure of Brady and McHugh;[3] it melted at 64–65°. The acetyl compound evidently was not particularly sensitive to acetic acid at 0°. However, it is necessary to exclude bright light, halogen acid fumes, etc.[2]

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[1] Presented at the Washington meeting of the American Chemical Society, March, 1933.

[2] A number of years ago Hantzsch [*Ber.*, **24**, 20 (1891)] reported that acetyl-β-aldoximes reacted with alkali carbonates to form nitriles, and with sodium or ammonium hydroxide to form the corresponding β-oxime. Later, Brady and Dunn [*J. Chem. Soc.*, **103**, 1625 (1913)] reported that certain acetyl-β-aldoximes reacted with alkali to form nitriles. See also Freudenberg "Stereochemie," 1933, [7] p. 975.

[3] Brady and McHugh, *J. Chem. Soc.*, **127**, 2423 (1925).

The acetyl derivatives of β-3,4-methylenedioxybenzaldoxime (m. p. 84–85°), β-3-nitrobenzaldoxime (m. p. 97–98°), and β-4-chlorobenzaldoxime (m. p. 86–87°) have been prepared in a similar manner. The melting points of the first two agreed approximately with those reported by Brady and McHugh[3] and not with those reported by Hantzsch. In general these substances were dried on a porous plate over potassium hydroxide in a vacuum desiccator and used within a short time after preparation.

Further evidence that these acetyl derivatives were essentially pure substances has been obtained in the following manner. When ether solutions of the acetyl derivatives of β-4-methoxybenzaldoxime and of β-3,4-methylenedioxybenzaldoxime were extracted with cold sodium hydroxide, and the alkaline layers saturated with carbon dioxide, only very small amounts of the corresponding oximes were obtained, whereas, when an ether solution of a β-oxime was extracted by alkali in a similar manner 80% of it was recovered. It was shown also that these acetyl derivatives neutralized approximately equivalents of standard alkali. After samples of the acetyl compounds in alcoholic solutions were allowed to stand with excess of standard alkali for twenty hours, the excess base was titrated with acid using phenolphthalein as indicator. The results in terms of 0.1 *N* alkali are given in Table I. The amounts of alkali neutralized were approximately equivalent to the quantities of acetic acid that would have been formed by the decomposition of pure samples of the acetyl compounds. Blanks were run with nitrile and oxime, the latter being too weak an acid to interfere with the titration for acetic acid under the conditions used. Also, a mixture consisting of two-thirds acetyl-β-4-methoxybenzaldoxime and one-third of the corresponding oxime neutralized an amount of standard alkali approximately equivalent to the amount of acetyl compound present in the mixture. The total error in this method of analysis was less than 3%.

TABLE I

Calcd. 0.3914 g. $CH_3OC_6H_4CH{=}NOCOCH_3$ = 20.3 cc. 0.1 *M* NaOH. Found, 20.1 cc.
Calcd. 0.1485 g. $CH_3OC_6H_4CH{=}NOCOCH_3$ = 7.69 cc. 0.1 *M* NaOH. Found, 7.70 cc.
Calcd. 0.8100 g. 3,4-$CH_2O_2C_6H_3CH{=}NOCOCH_3$ = 39.1 cc. 0.1 *M* NaOH. Found, 38.4 cc.

Yields of Products from Acetyl-β-aldoximes and Alkali.—Following the general procedure of Brady and McHugh[3] certain acetyl derivatives were shaken with 2 *N* aqueous sodium hydroxide at 0°, kept for twenty to forty minutes and filtered. The solid was the corresponding nitrile. The corresponding β-oxime was precipitated from the filtrate by passing in carbon dioxide or by adding concentrated ammonium chloride. The experiments were repeated at 30°. The average yields of nitriles and oxime obtained from several runs together with the melting points of the products are given in Table II. The products were identified by determining mixed melting points with authentic specimens of the nitrile and β-oxime.

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(4) See Hantzsch, *Z. physik. Chem.*, **13**, 511 (1894).

The yields of products have been determined also from the reaction of 0.125–0.25 *M* acetyl aldoxime with 0.5 *M* alkali in 95% alcoholic solution. After standing for twenty to twenty-four hours the solution was evaporated to dryness at room temperature by means of a hood draft. The residue was triturated with 10 cc. of 2 *N* sodium hydroxide and filtered through a Gooch crucible. The oxime was precipitated from the filtrate with carbon dioxide, and filtered through another Gooch crucible. No appreciable amount of organic acid was obtained by acidifying the bicarbonate solution. The products were washed, dried and weighed. The yields are given in Table III.

TABLE II

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-β-BENZALDOXIMES AND AQUEOUS ALKALI

Acetyl derivative	Temp., °C.	Nitrile	Oxime	Total
4-Methoxy-	0	25 (m. p. 56–57°)	63 (m. p. 125–128°)	88
3-Nitro-	0	33 (m. p. 114–116°)	40 (m. p. 108–112°)	73
4-Methoxy-	30	55 (m. p. 56–57°)	30 (m. p. 125–128°)	85
3-Nitro-	30	52 (m. p. 114–116°)	25 (m. p. 108–113°)	77

TABLE III

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-β-BENZALDOXIMES AND ALKALI IN ALCOHOLIC SOLUTION

Acetyl derivative	Temp., °C.	Nitrile	Oxime	Total
4-Methoxy-	0	35 (m. p. 57–59°)	56 (m. p. 124°)	91
4-Chloro-	0	35 (m. p. 83°)	60 (m. p. 146°)	95
3,4-Methylenedioxy-	0	22 (m. p. 87–90°)	56 (m. p. 135–138°)	78
4-Methoxy-	30	68 (m. p. 57°)	31 (m. p. 123–124°)	99
4-Chloro-	30	67	30 (m. p. 147°)	97
3,4-Methylenedioxy-	30	64 (m. p. 87–90°)	25 (m. p. 132–134°)	89

Reaction of Acetyl-β-aldoximes with Sodium Carbonate.—The only product that could be isolated from the reaction of acetyl-β-4-methoxybenzaldoxime or acetyl-β-3-nitrobenzaldoxime with aqueous sodium carbonate at 0 or 30° was the corresponding nitrile, in yields of 70–90% of the theoretical quantities.

Summary

It has been shown that certain acetyl-β-aldoximes react with sodium hydroxide to form partly nitrile and partly β-oxime.

DURHAM, N. C.

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The Action of Elementary Fluorine upon Certain Aromatic Organic Compounds under Various Conditions. I

BY LUCIUS A. BIGELOW, J. HERBERT PEARSON, LOUIS B. COOK AND WILLIAM T. MILLER, JR.

Fluorine is the most reactive, as well as the most electronegative, of all the elements, and it is surprising, therefore, to find that the direct fluorination of organic compounds has received scant attention from earlier investigators.[1] This is due in part to the enormous reactivity of the fluorine, which combines explosively with most organic compounds when the two are brought in contact; and in part also to the fact that the reactions of free fluorine, at least upon aromatic compounds, do not seem to follow well-recognized lines which might be predicted by analogy and studied readily. The work to be described in this paper represents the initial stage of a careful study of the controlled reactions of elementary fluorine upon a variety of aromatic organic compounds, under a number of differing types of experimental conditions.

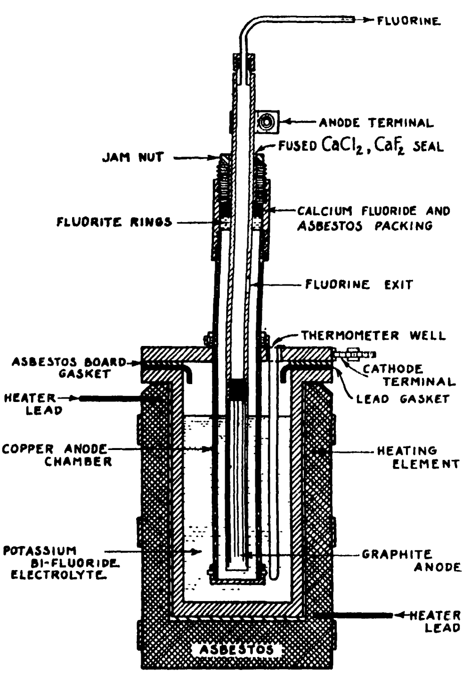

Fig. 1.—Fluorine generator.

The Apparatus

The fluorine was generated by the electrolysis of molten potassium bifluoride, at 250–300°, in an electrolytic cell made of heavy copper, and illustrated in detail in Fig. 1. This generator was designed several years ago by Paul M. Gross and J. S. Buck in this Laboratory, and was similar in principle to several which have been described previously in the literature. It differed significantly from these, however, in that the copper pipe which held the graphite anode also served as the exit for the fluorine, and was supported by means of a fluorite ring, which was both insulating, and entirely inert, even under severe operating conditions. The gas, after being set free at the anode, was passed through a copper tube approximately 63 × 3.5 cm. filled with anhydrous

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(1) The most important literature references are as follows: Moissan, *Compt. rend.*, **102**, 1543 (1886); **103**, 202, 256, 600 (1886); Humiston, *J. Phys. Chem.*, **23**, 572 (1919); Fichter and Humpert, *Helv. Chim. Acta*, **9**, 692 (1926); Bancroft and Jones, *Trans. Electrochem. Soc.*, **53**, 183 (1929); Bancroft and Whearty, *Proc. Nat. Acad. Sci.*, **17**, 183 (1931); Whearty, *J. Phys. Chem.*, **35**, 3121 (1931); Ruff and Keim, *Z. anorg. Chem.*, **201**, 245 (1931).

sodium fluoride, in order to remove quantitatively[2] any hydrogen fluoride which it might contain. From a charge of 2 kg. the generator delivered a steady flow of nearly pure fluorine for about 35 hours, using an electrolyzing current of 5 amp. at a potential of 8–10 volts.

In our first experiments, the fluorine was passed directly into carbon tetrachloride solutions of the materials to be tested, contained in a three-necked Pyrex flask, closed with rubber stoppers, equipped with a mechanical stirrer of the ordinary type, and immersed in an efficient ice bath. The glass proved surprisingly resistant and the stoppers did not burn, but the arrangement was not so satisfactory in cases where explosions might occur.

Then it was found that a brass reaction vessel was quite as suitable as one of glass, being even more resistant, essentially unbreakable, and without effect upon the course of the reactions involved. It was made from a piece of 10-cm. heavy duty brass pipe, 18 cm. long, with a bottom soldered in; and had an inset lid, which carried a metal bearing for a copper stirrer, and copper inlet and outlet tubes for the fluorine. The lid was held in place by means of springs, so that even in the event of an explosion no damage could be done to the apparatus or the operator.

In the preliminary work it was noticed that the reactions were always accompanied by occasional bright flashes of light, which appeared in the vapor phase, either within the inlet tube or above the solution. It was thought, therefore, that if the vapor phase were essentially eliminated, not only the flashing but also all detonations might be prevented. Accordingly, an apparatus was designed to accomplish this. It was made of heavy copper, and is illustrated in detail in Fig. 2. The diagram is self-explanatory, but certain features of the design may perhaps be mentioned especially. The lid, provided with a ground joint, was held in place by springs, and had only two openings. One of these was for the stirrer, and the other for the inlet and outlet tubes for the fluorine, one of which was inside the other. The stirrer was activated by a jet of air playing on a paddle wheel, and the bearing in which it turned was so arranged as to be sealed from the action of the fluorine when the apparatus was full of liquid.

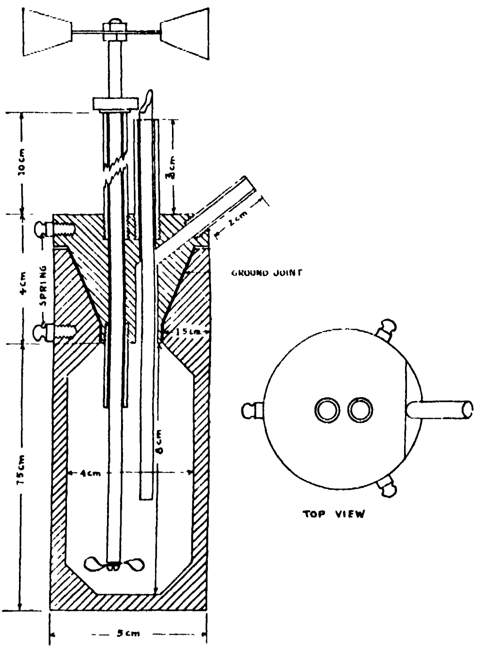

Fig. 2.—Copper reaction vessel.

Discussion of Procedure and Results

In carrying out a study of the direct action of elementary fluorine upon aromatic organic compounds, the first problem which had to be met was that of controlling the reaction. From a survey of the literature, it appeared that this would be extremely difficult, but it soon was found that

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(2) Dennis, Veeder and Rochow, THIS JOURNAL, **53**, 3263 (1931).

numerous organic compounds, either dissolved or suspended ed carbon tetrachloride, could be exposed to the action of the g ny hours in succession without the slightest danger, provided that the mixtures were kept at 0°, and adequately stirred. Not only this, but the halogen could be passed directly into certain aromatic organic liquids at temperatures as high as 25° without danger under similar conditions, provided also that no significant vapor phase was present. It seems, therefore, that these reactions are much easier to handle than has been supposed heretofore. However, it is important to bear in mind that the simple conditions just described *must* be fulfilled. Otherwise disastrous explosions may occur without warning, involving a significant degree of danger to the operator.

Fluorine has been shown unquestionably to liberate chlorine from carbon tetrachloride at 0°, contrary to the statement of Ruff and Keim,[1] and in a sufficiently active state to chlorinate dissolved *toluene* to form hexachlorobenzene over a period of a few hours. The displacement is rather slow, however; and if a compound is present in the solution which will react with the fluorine at a more rapid rate, it will be fluorinated only. Otherwise it will be both fluorinated and chlorinated. These observations show that the statement by Ruff and Keim already alluded to can no longer be accepted without qualification.

When the gas was passed into a solution of naphthalene in carbon tetrachloride, 3% by weight, at 0°, a dark colored precipitate was formed, which, after being filtered off and dried, became light gray. It was amorphous in character, could not be crystallized from any ordinary solvent and could be purified only in part by precipitating its solution in ether by the addition of ligroin. The material, which seemed to be a polymerized addition product, was not very stable, melted after purification at 176–177° (decomp.) and was found upon analysis to contain considerable fluorine and but little chlorine. The progressive fluorination of such a solution, for six-hour periods, yielded first a gray material, containing 37.7% F, and decomposing at 98–104°; then a yellowish one with 45.9% F, decomposing at 158–170°; and finally a white powder, quite stable in air, with no less than 52.4% F, decomposing at 148–155°. The figures are average checked values. This procedure removed the naphthalene quantitatively from the carbon tetrachloride solution. The white product thus otained was found to possess some sufficiently remarkable properties. When dissolved in ether and treated with sodium carbonate solution, it was decomposed readily, but it could be boiled for several hours with fuming nitric acid, in which it was quite soluble, and yet be recovered not greatly changed. When subjected to this latter treatment, the fluorine content of the material progressively increased, until finally there was obtained a white powder which contained no less than 57.4% F.

Oxidation of the fluorinated naphthalene by means of alkaline permanganate solutions at 20, 50 and 100° failed to yield either phthalic acid or any of its derivatives, but the sample was mostly destroyed in each case. Acid permanganate solutions gave no better results, while chromic anhydride in acetic anhydride solution at 70° did not oxidize the material at all. Furthermore, catalytic reduction with hydrogen under pressure in the presence of a platinum catalyst did not change the material, whereas fluorobenzene could be reduced readily to cyclohexane by this treatment.

The question soon arose as to whether the formation of this type of fluorinated product was a property of naphthalene alone, or of the naphthalene ring system. It was found that α-methylnaphthalene yielded a fluorinated product containing 30.7% F; β-methyl-, 27.2%; α-methoxy-, 33.3%; β-methoxy-, 30.4%; α-hydroxy-, 30.4%; β-hydroxy-, 29.8%; α-nitro-, 34.4%; α-bromo-, 35.9%; tetrahydro-, 26.4%. These materials were similar in properties to that obtained from the parent hydrocarbon, and all decomposed from approximately 90–110°. Also, decahydronaphthalene yielded no derivative of this type. This fact is significant, as it indicates clearly that the reaction is a property of the aromatic organic nucleus, as distinguished from the cycloparaffins. It is interesting to note that neither the nitro group nor the bromine atom was displaced completely by the fluorine, and the α-nitro derivative gave the highest yield. Also, the α-derivatives gave in every case a higher yield than the corresponding β-compounds, under comparable conditions.

Turning now to another phase of the work, it has been found that certain derivatives of dibenzyl gave fluorinated compounds of a type similar to those just described. When fluorine was passed into suspensions of benzoin, desoxybenzoin, dibenzoylmethane, or benzil in carbon tetrachloride at 0° in the absence of a vapor phase, reaction occurred, and the materials in suspension were replaced gradually by fluorinated products. These were gray to white amorphous solids, decomposing from 115–150°, and which could not be crystallized, but could be purified in part only, by the ether–ligroin treatment. They contained, in the order named, 25.6, 31.2, 30.7, 30.5% F; and 1.3, 6.4, 8.6, 2.2% Cl. The more readily enolizable hydrogen atom there was in the original material, the higher the chlorine content of the fluorinated product, showing that chlorination was taking place mostly along well-recognized lines; but the fluorine content followed no such order, indicating, at any rate, that the fluorination was taking place by a different mechanism. This idea was supported by the fact that the product obtained from benzil, which contains no hydrogen at all in the chain, contained much fluorine, and but little chlorine.

The product obtained from desoxybenzoin, like the naphthalene derivatives, was sensitive, when dissolved in ether, to sodium carbonate solution, and resistant to fuming nitric acid. When it was boiled with the latter reagent, however, about three-fourths of the sample was recovered, but it had lost about one-third of its fluorine content in the process. The presence of vanadium pentoxide as a catalyst did not have any effect. No benzoic acid, or any of its derivatives, could be detected among the oxidation products, which is a strong indication that both of the aromatic rings present were involved in the reaction.

The fluorinated material discussed thus far was totally different in character from the numerous fluorine substitution products which have been prepared by indirect methods and described in the literature. The products seemed to be polymerized, but numerous attempts to determine their molecular weights were unreliable, since their solutions were usually colloidal. The question as to whether these materials still retained their original carbon skeletons, or whether they consisted of highly polymerized aliphatic fragments, cannot be answered definitely at the present time; but indications are that a general breakdown of the molecular structure did not take place during the fluorinations.

The situation was quite different from what has been outlined above, when a monocyclic aromatic hydrocarbon, such as toluene, was fluorinated in carbon tetrachloride solution, 15% by volume, at 0°. The reaction was carried out in the presence of a trace of iodine. In this case no precipitation, other than that of a little free carbon, occurred, and the reaction apparently took place at a very much slower rate than before. A dark colored, fuming solution was obtained, which obviously contained unstable products, as it underwent color changes when neutralized. After the removal of the solvent, and most of the excess of toluene, a highly unstable liquid product remained, which was difficult to deal with. However, if the mixture was boiled with alkali just previous to the removal of the excess of hydrocarbon, then a stable dark red oil was formed, which could be distilled without difficulty under reduced pressure. The material was first fractionated in the ordinary way and separated into a light yellow oil, a white crystalline solid, and a considerable tarry residue. The solid, much to our surprise, turned out to be hexachlorobenzene, showing that nascent chlorine, in the presence of fluorine, was sufficiently active to chlorinate the ring completely even at 0°, and to remove the methyl group as well.

The oil was redistilled at 4 mm. in the usual manner, and then continuously fractionated at 4 mm., using a Hickman Auto-Vac Still, provided with attachments for introducing and withdrawing samples from the system without disturbing the vacuum. This procedure was continued until it was evident that no complete separation could be obtained by distillation with the apparatus at our disposal. The lowest boiling fraction was a colorless oil, boiling at 54–57° at 4 mm. and was shown by analysis and oxidation to consist largely of *p*-chlorotoluene. The other four were mixtures and boiled from 74–100, 100–121, 118–129 and 128–138°, respectively, at 4 mm. In the same order, their average molecular weights were 153, 212, 227 and 244. They contained 10.8, 14.0, 12.0, 7.8% F and 38.5, 43.4, 47.4, 52.7% Cl. Thus the molecular weight and the chlorine content rose progressively with the boiling point, while the fluorine content at first rose and then fell off again.

An analysis of the analytical figures shows, first, that no significant degree of polymerization could have taken place in this case, if it is assumed that the products were in any sense derivatives of toluene. Also, since the halogen content and the molecular weight of each fraction were known, the ratio of fluorine to chlorine in each could be calculated. The values were 1:2; 1:2; 1:1.7 and 1:3.6, in the order of increasing boiling points.

Oxidative degradation of these materials with potassium permanganate in alkaline solution, or chromic anhydride in acetic anhydride solution, destroyed the fluorine-containing constituents of the samples; while catalytic reduction did not remove any appreciable quantity of fluorine from the compounds. Alcoholic potassium hydroxide solution removed about 36% of the chlorine present in the mixed distillates, but none of the fluorine, which fact lends support to the idea that the latter halogen was not present in an additive condition. Furthermore, no oxalic acid was found in the filtrates obtained in the last procedure, from which it seems unlikely that a complete hydrolysis of the highly halogenated molecules had occurred.

It is obvious from the reactions just described that the chlorine set free from the solvent by the fluorine was a complicating and undesirable factor. Also, it had been found that the flashing and very likely the explosions which had occurred took place entirely in the vapor phase. Consequently, the copper apparatus already described was designed, and fluorine was passed directly into liquid toluene in the absence of any considerable vapor phase, at temperatures even as high as 25°. Under these conditions there was no sign of explosion or of flashing, and the fluorine could be passed through the hydrocarbon for hours without the slightest difficulty. Vigorous reaction took place, however, accompanied by the evolution of smoke, and the deposition of free carbon, but the recovered toluene contained no fluorine. In several experiments various halogenation catalysts, including iodine, iron powder, antimony fluoride, ferric fluoride and aluminum chloride were used, but entirely without effect, in one case even after twenty-four consecutive hours of fluorination at 0°. Nitrobenzene, dimethylaniline and acetophenone were tried also, but, although the reactions could be controlled easily, they approximated incomplete combustion, and the recovered compounds contained no halogen. In spite of these negative results, however, it is believed that this controlled fluorination has far-reaching possibilities, and it represents, to the best of the writers' knowledge, the first time that it has been possible to pass fluorine through relatively large quantities of organic liquids over considerable periods of time in complete safety.

The analytical method for the estimation of fluorine used in this work was a modification of that recommended by Vaughn and Nieuwland.[3] The halogen was weighed as calcium fluoride, which was previously washed with acetone and heated to constant weight at 160–170°. A correction of 17 mg. per liter was made to allow for the solubility of calcium fluoride in water. The method gave results within 0.5% of the calculated values as shown by the analysis of pure *p*-fluorobenzoic acid.

The results described in the preceding paragraphs show that the action of elementary fluorine on various aromatic organic compounds can be controlled without difficulty, and leads to a variety of interesting and significant products. They are presented at this time as the beginning of an attack upon the general, and very difficult, problem of the mechanism of the action of elementary fluorine upon the aromatic organic nucleus. The work is to be continued actively in this Laboratory.

We are pleased to acknowledge here the friendly interest of Dr. Paul M. Gross, who originally suggested this line of investigation, and who has contributed many valuable suggestions as the work has progressed.

Summary

Several procedures have been described for reaction of elementary fluorine with various aromatic organic compounds, and two types of metal apparatus designed for this purpose.

The action of fluorine on toluene, naphthalene, and twelve naphthalene derivatives, in carbon tetrachloride solution, has been investigated; and products containing over 50% of fluorine isolated.

A study has been made of the action of fluorine on a number of derivatives of dibenzyl in carbon tetrachloride suspension.

Free fluorine has been passed directly through certain organic liquids, at temperatures as high as 25° in the absence of any significant vapor phase. No violent reaction occurred under these conditions although free carbon was deposited.

DURHAM, NORTH CAROLINA

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PUBLISHED NOVEMBER 7, 1933

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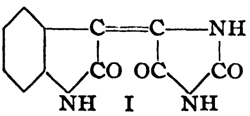
(3) Vaughn and Nieuwland, *Ind. Eng. Chem.*, *Anal. Ed.*, 3, 274 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Hydrolysis and Reduction of Hydantoin-Oxindoles[1]

BY HENRY R. HENZE AND CHARLES M. BLAIR

The only recorded instance of the direct hydrolysis of an unsaturated hydantoin-carbonyl compound is that of anisalhydantoin,[2] the action of barium hydroxide producing *p*-methoxyphenylpyruvic acid. The primary purpose of this investigation was to study the direct hydrolysis of hydantoin-$\Delta^{5,3'}$-oxindole (I) and its 5′-methyl homolog (II). Since a supply of (I) was available it was possible to repeat the conflicting researches of Kotake[3] and of Hill and collaborators[4] and thus to establish the structure of the quinolone acid obtained by the reduction and hydrolysis procedures. With the exception of a minor difference in one melting point, the results of the latter investigators have been verified. On the contrary, Kotake's synthesis of 2,3-dihydroxy-3,4-dihydroquinoline-4-carboxylic acid could not be confirmed.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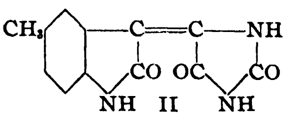
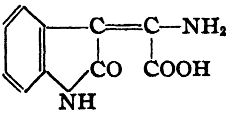

II

From a knowledge of the behavior of the hydantoin and oxindole groupings, respectively, toward alkali it would seem possible to predict one or more of the following compounds as the reaction product of the interaction of barium hydroxide and hydantoin-$\Delta^{5,3'}$-oxindole (I)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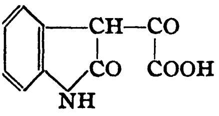
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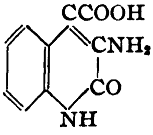
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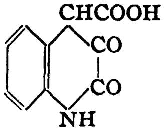
VI

If normal cleavage of the hydantoin ring, unaccompanied by any change in the oxindole portion of the molecule, should take place the resulting product would be the unsaturated alpha amino acid, $C_{10}H_8N_2O_3$ (III). If, however, in addition to the usual decomposition of the hydantoin nucleus the amino group was eliminated by hydrolysis, the compound thus produced would be a substituted pyruvic acid, $C_{10}H_7NO_4$ (IV). Finally, since it is known that the oxindole nucleus is opened by alkali and that subsequent ring closure, upon acidification, would favor the formation of a six rather than a five-membered ring, it might be expected that hydrolysis

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(1) This paper is from a portion of the dissertation submitted by Charles M. Blair to the faculty of the University of Texas, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1933.

(2) Wheeler and Hoffman, *Am. Chem. J.*, **45**, 368 (1911).

(3) Kotake, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **6**, 61 (1927).

(4) Hill, Schultz and Lindwall, THIS JOURNAL, **52**, 769 (1930).

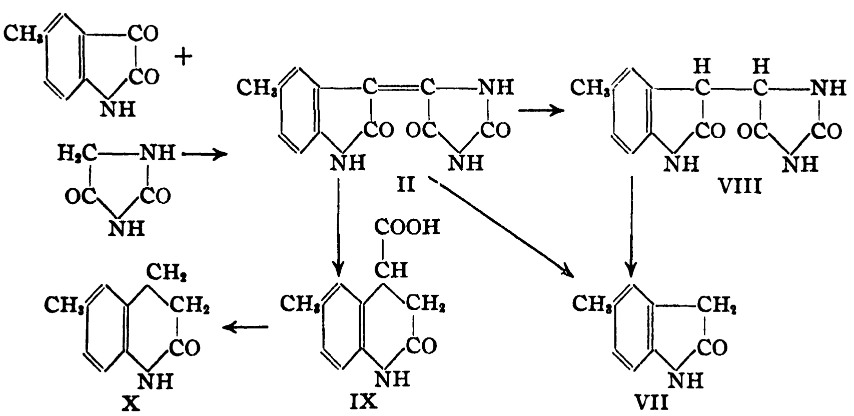
would result in the formation of a quinolone carboxylic acid, either $C_{10}H_8N_2O_3$ (V) or $C_{10}H_7NO_4$ (VI), according to whether or not an amino group was eliminated during the reaction.

The hydrolysis of hydantoin-$\Delta^{5,3'}$-oxindole proceeded in a manner totally different from those outlined above in that a compound of the molecular formula C_8H_7NO was formed. Hence, during the hydrolysis not only had the usual decomposition of the hydantoin ring taken place, but, in addition, cleavage had occurred at the double bond thus removing a fragment containing two carbon atoms. This fact was established by identifying oxalate in the reaction residue.

As the hydrolysis product agreed in empirical formula and in melting point with these properties recorded for oxindole, the latter was synthesized by the method of Marschalk[5] and comparison of it with the compound C_8H_7NO indicated that the two substances were identical. Since the formation of oxindole was so unexpected further substantiation of this structure was obtained by converting the hydrolysis product into isatoxime and final proof was secured by synthesizing monobromo oxindole from it.

In complete analogy to the foregoing the condensation product of hydantoin and 5-methylisatin upon treatment with barium hydroxide solution yielded 5-methyloxindole (VII).

Reduction of hydantoin-$\Delta^{5,3'}$-5'-methyloxindole (II), catalytically or by means of hydriodic acid, led smoothly to the formation of the anticipated compound, hydantoin-(5,3')-5'-methyloxindole (VIII). The latter on hydrolysis by means of barium hydroxide and subsequent acidification formed 5-methyloxindole (VII) rather than a quinolone carboxylic acid. However, when the hydantoin-$\Delta^{5,3'}$-5'-methyloxindole was treated with hydriodic acid in the presence of red phosphorus 2-keto-6-methyl-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (IX) resulted.



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[5] Marschalk, *Ber.*, **45**, 584 (1912).

Experimental

Hydrolysis of Hydantoin-$\Delta^{5,3'}$-oxindole.—Sixty-eight grams of hydantoin-$\Delta^{5,3'}$-oxindole (I), 510 g. of barium hydroxide and 510 cc. of water were digested in an oil-bath at 115–120° under reflux condenser until ammonia was no longer evolved. Five hundred cubic centimeters of boiling water was added and the barium removed with carbon dioxide and the required amount of sulfuric acid. The presence of oxalate in the precipitated barium salts was established. The filtrate was acidified with glacial acetic acid and evaporated to dryness. Recrystallization of the residue from water produced 25 g. of colorless needles melting sharply at 127° (corr.). Analysis of the purified product indicated that its formula was C_8H_7NO.

Anal. Calcd. for C_8H_7NO: C, 72.15; H, 5.30; N, 10.52; mol. wt., 133. Found: C, 72.00, 72.05; H, 5.12, 5.16; N, 10.54, 10.64; mol. wt. (in freezing glacial acetic acid), 134.

When the compound C_8H_7NO was mixed with oxindole[5] of known purity, which melted at 127° (corr.), the resulting mixture melted unchanged at the same temperature.

The action of nitrous acid on the product C_8H_7NO yielded an oxime, $C_8H_6N_2O_2$, which melted at 202° (corr.) and which corresponded in all respects with isatoxime.

Anal. Calcd. for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.45; H, 3.99; N, 17.42.

A cold aqueous solution of C_8H_7NO was acidified and treated with a volume of Koppeschaar's solution equivalent to one molecular proportion of bromine. The colorless prisms which separated after recrystallization from water and from alcohol melted with decomposition at 220–221° (corr.).[6] The results of the analyses established the molecular formula C_8H_6ONBr corresponding to that of a monobromoxindole.

Anal. Calcd. for C_8H_6ONBr: C, 45.28; H, 2.99; N, 6.61; Br, 37.70. Found: C, 45.24; H, 2.86; N, 6.54; Br, 37.96.

Hydantoin-$\Delta^{5,3'}$-5'-methyloxindole (II).—This compound was obtained by heating 80.5 g. of 5-methylisatin, 50 g. of hydantoin, 100 g. of fused sodium acetate and 500 cc. of glacial acetic acid (containing 20 g. of acetic anhydride) in an oil-bath at 150° for five hours. The usual procedure for hydantoin condensations was followed and yielded 78 g. of a reddish-brown solid of melting point above 310° and insoluble in all the common solvents except alkaline solutions.

Anal. Calcd. for $C_{12}H_9O_3N_3$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.42; H, 3.84; N, 17.37.

Hydrolysis of Hydantoin-$\Delta^{5,3'}$-5'-methyloxindole (II).—Twenty-three grams of (II), 173 g. of barium hydroxide and 173 cc. of water were refluxed in an oil-bath at 115–120° for two days, ammonia being evolved. Here, too, the residue of barium salts gave a positive test for oxalate. The purified product, weighing 4 g. and consisting of colorless crystals melting at 175° (corr.),[7] was 5-methyloxindole.

Anal. Calcd. for C_9H_9ON: C, 73.43; H, 6.12; N, 9.52. Found: C, 73.26; H, 6.10; N, 9.65.

2-Quinolone-4-carboxylic Acid. A.—Following the method of Hill, Schultz and Lindwall, hydantoin-$\Delta^{5,3'}$-oxindole was reduced forming hydantoin-$(^{5,3'})$-oxindole (which was found to melt at 281–282° (corr.) (dec.) instead of at 276°) which upon hy-

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(6) Since the melting point reported by von Baeyer and Knopp [*Ann.*, **140**, 1 (1866)] for monobromoxindole is 176°, this compound was resynthesized by treating oxindole with bromine water. The melting point of the monobromoxindole thus obtained, as well as a mixture of it with the C_8H_6ONBr, was 220–221° (corr.) with decomposition.

(7) M. p. given as 168° by Reissert and Scherk [*Ber.*, **31**, 393 (1898)], by Wahl and Faivert [*Ann. chim.*, **5**, 314 (1926)] and by Stollé, Bergdoll, Luther, Auerhahn and Wacker, *J. prakt. Chem.*, **128**, 1 (1930).

drolysis with barium hydroxide was converted into 2-quinolone-4-carboxylic acid thus confirming the work of these investigators.

B. Isatin and hydantoin were condensed according to the method of Kotake forming 1-acetyl-hydantoin-$\Delta^{5,3'}$-1'-acetyloxindole, which Kotake described as charring at 245° but which in this investigation was found to sinter at 240–245° and to melt with decomposition at 258° (corr.). Reduction of this diacetyl derivative by means of zinc and acetic acid produced hydantoin-(5,3')-1'-acetyloxindole melting at 248° (corr.) [K.—m. p. about 243°].[8] The melting point of hydantoin-(5,3')-oxindole obtained by solution of the monoacetyl derivative in dilute sodium hydroxide and subsequent acidification was 281–282° (corr.) [K.—m. p. 283–284°]. When the directions recorded by Kotake for the hydrolysis of hydantoin-(5,3')-oxindole were followed explicitly the compound obtained was 2-quinolone-4-carboxylic acid and not 2,3-dihydroxy-3,4-dihydroquinoline-4-carboxylic acid.

Hydantoin-(5,3')-5'-methyloxindole (VIII).—A suspension of 50 g. of hydantoin-$\Delta^{5,3'}$-5'-methyloxindole, 225 cc. of hydriodic acid (sp. gr. 1.7) and 500 cc. of glacial acetic acid was boiled gently in an oil-bath for one hour. When all solids had dissolved, the solution was steam distilled to remove acid, chilled in an ice-bath and the separated product filtered off and washed with water and acetone. The dried residue, weighing 26 g., was recrystallized from water yielding snow white silky needles melting with decomposition at 306–307° (corr.).

Anal. Calcd. for $C_{12}H_{11}O_3N_3$: C, 58.78; H, 4.49; N, 17.14. Found: C, 58.95; H, 4.61; N, 17.32.

For the preparation of small quantities of VIII catalytic reduction using Adams platinum catalyst with alcohol as the solvent was very satisfactory.

Hydrolysis of Hydantoin-(5,3')-5'-methyloxindole.—Twenty-three grams of VIII, 173 g. of barium hydroxide and 173 cc. of water were heated for two days in an oil-bath at 115–120°. Barium compounds were removed in the usual manner and gave a positive test for the presence of oxalate. The filtrate was evaporated to dryness, the residue upon recrystallization from water yielding 4 g. of small, nearly colorless needles melting at 175°. A mixture of this product with 5-methyloxindole melted at the same temperature.

Anal. Calcd. for C_9H_9ON: C, 73.43; H, 6.12; N, 9.52. Found: C, 73.36; H, 6.18; N, 9.39.

2-Keto-6-methyl-1,2,3,4-tetrahydroquinoline-4-carboxylic Acid (IX).—Eight grams of hydantoin-$\Delta^{5,3'}$-5'-methyloxindole, 5 g. of red phosphorus and 50 cc. of hydriodic acid (sp. gr. 1.7) was heated for seven hours in an oil-bath at 150°. The mixture was steam distilled, filtered from phosphorus, decolorized and cooled. The product was recrystallized from water yielding 2 g. of colorless needles melting at 219–220° (corr.). This melting point is not changed by mixing the compound with a sample of 2-keto-6-methyl-1,2,3,4-tetrahydroquinoline-4-carboxylic acid of known purity.

Anal. Calcd. for $C_{11}H_{11}O_3N$: C, 64.37; H, 5.41; N, 6.86. Found: C, 64.22; H, 5.33; N, 6.73.

This acid was decarboxylated by dry distillation with barium hydroxide forming 2-keto-6-methyl-1,2,3,4-tetrahydroquinoline (X) which melted at 114–115° (corr.).[9]

Summary

1. The action of barium hydroxide solution on the condensation products of hydantoin with isatin and 5-methylisatin completely destroyed the

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(8) Concerning this reduction product Kotake's statement is extremely confusing in that, while the analyses reported agreed quite well with $C_{14}H_{13}O_4N_3$, he concluded that "the analytical results indicated $C_{11}H_{13}O_3N_4$ representing no conceivable formula."

(9) M. p. given as 106° by Mayer, van Zütphen and Phillips, *Ber.*, 60B, 858 (1927).

hydantoin nucleus and reduced the isatin portion to the corresponding oxindole.

2. Toward barium hydroxide solution hydantoin-5,3′-oxindole and its 5′-methyl homolog differ in their behavior in that the former is converted into 2-quinolone-4-carboxylic acid and the latter into 5-methyloxindole.

3. The synthesis of 2-quinolone-4-carboxylic acid by Hill, Schultz and Lindwall has been confirmed, whereas the conflicting research of Kotake has, in part, been shown to be in error.

AUSTIN, TEXAS

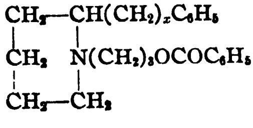
RECEIVED JULY 13, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

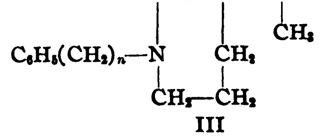
Piperidine Derivatives. XIII. Phenyl and Phenylalkyl Substituted Piperidinopropyl Benzoates

BY L. A. WALTERS AND S. M. MCELVAIN

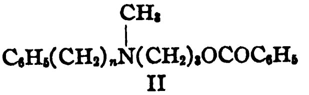
In a previous paper[1] the unusual local anesthetic action of compounds of type I on mucous surfaces was reported. Since the substances in which x is 1 and 2 were many times more effective as anesthetics than the compound in which a phenylethyl group substitutes the 4 position of the piperidine nucleus, it appeared that there might be an optimum position of the phenyl group relative to the nitrogen atom for maximum anesthetic action. In subsequent work an effort was made to test this possibility by the preparation of series of anesthetics of types II[2] and III[3] in which the number of carbon atoms separating the nitrogen atom from the phenyl group was varied from 1 to 5. However, compounds of type II and III proved to be so irritating to the mucous surfaces (rabbit's cornea) that no definite conclusion could be drawn in this connection.



I



III



$$C_6H_5(CH_2)_n\overset{CH_3}{\overset{|}{N}}(CH_2)_3OCOC_6H_5$$

II

It therefore seemed desirable to extend the study to structures of type I. The present paper reports the preparation and properties of the 2-phenyl-

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(1) Bailey and McElvain, THIS JOURNAL, 52, 1633 (1930).

(2) Cope and McElvain, *ibid.*, 53, 1587 (1931).

(3) Strong and McElvain, *ibid.*, 55, 816 (1933).

(x = 0) 2-phenylpropyl-(x = 3), 2-phenylbutyl-(x = 4), 3-phenyl-, 3 benzyl- and 4-phenyl-piperidinopropyl benzoates. The compounds were prepared by the condensation of γ-chloropropyl benzoate with the appropriately substituted piperidines, the preparations of which are described in the experimental part.

Experimental

Phenyl and Phenylalkyl Pyridines.—2-Phenylpyridine was prepared in 40% yield by the method of Ziegler and Zeiser,[4] in which the following modification was used. In order that the heating of the ethereal solution of lithium phenyl and pyridine in a sealed tube might be avoided, the ether was removed by distillation and simultaneously replaced by toluene. The decomposition into lithium hydride and 2-phenylpyridine took place readily when the toluene solution was heated to 100° for four hours; b. p. 270–272° (740 mm.); m. p. of picrate 173–174°; reported by Ziegler and Zeiser,[4] 175°.

2-(γ-Phenylpropyl)- and 2-(δ-phenylbutyl)-pyridine were prepared by the action of γ-phenylpropyl bromide and δ-phenylbutyl bromide on lithium picolyl.[5] In these preparations it was found necessary to add the phenylalkyl bromide to the reaction mixture immediately after the addition of the α-picoline to the lithium butyl had been completed. If the addition of the bromide is delayed, even for a short time, the yield of the phenylalkyl pyridines is very materially lowered. The properties and yields of these new substituted pyridines that were prepared are summarized in Table I.

4-Phenylpyridine was prepared in 28% yields by the procedure of Forsyth and Pyman;[6] b. p. 266–269° (730 mm.); m. p. 74°.

Attempts to prepare 3-phenylpyridine by the method of Ciamician[7] as well as by the procedure of Pictet[8] were unsuccessful. A small amount of impure 3-phenylpyridine was obtained by the decarboxylation of *o*-β-pyridylbenzoic acid,[9] but this procedure was finally abandoned as impractical.

Phenyl- and Phenylalkylpiperidines.—The above-mentioned pyridines were reduced catalytically in methylcyclohexane solution over a nickel catalyst at 150° and under a pressure of 2000 pounds of hydrogen to the corresponding piperidines. 3-Benzylpiperidine was likewise prepared by the catalytic reduction of 3-benzoylpyridine.[10] The authors are indebted to Mr. B. H. Wojcik of this Laboratory for carrying out these reductions.

TABLE I

CERTAIN PHENYL AND PHENYLALKYL SUBSTITUTED PYRIDINES

Substituent	B. p., °C. mm.	Yield, %	d^{25}_{25}	n^{25}_{D}	Analyses, N, % Calcd.	Found
2-(γ-Phenylpropyl)	132–135 (2)	20	1.0171	1.5571	6.91	7.10
2-(δ-Phenylbutyl)	142–145 (2)	25	1.0040	1.5472	6.63	6.99

Since it was not possible to obtain 3-phenylpyridine in sufficient quantities to allow for its reduction to 3-phenylpiperidine, this latter compound was prepared by the following series of reactions

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(4) Ziegler and Zeiser, *Ber.*, **63**, 1849 (1930).

(5) Ziegler and Zeiser, *Ann.*, **485**, 192 (1931).

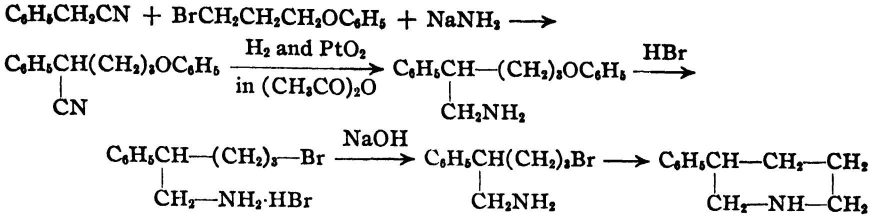
(6) Forsyth and Pyman, *J. Chem. Soc.*, 2922 (1926).

(7) Ciamician, *Ber.*, **20**, 192 (1887).

(8) Pictet, *ibid.*, **38**, 1946 (1905).

(9) Skraup and Cobenzl, *Monatsh.*, **4**, 456 (1883).

(10) LaForge, THIS JOURNAL, **50**, 2484 (1928).



$$C_6H_5CH_2CN + BrCH_2CH_2CH_2OC_6H_5 + NaNH_2 \longrightarrow$$

$$\underset{\displaystyle CN}{C_6H_5CH}(CH_2)_3OC_6H_5 \xrightarrow[\text{in } (CH_3CO)_2O]{H_2 \text{ and } PtO_2} \underset{\displaystyle CH_2NH_2}{C_6H_5CH}—(CH_2)_3OC_6H_5 \xrightarrow{HBr}$$

$$\underset{\displaystyle CH_2—NH_2{\cdot}HBr}{C_6H_5CH}—(CH_2)_3—Br \xrightarrow{NaOH} \underset{\displaystyle CH_2NH_2}{C_6H_5CH}(CH_2)_3Br \longrightarrow \begin{array}{l} C_6H_5CH—CH_2—CH_2 \\ \;\;|\qquad\qquad\qquad\;\; | \\ CH_2—NH—CH_2 \end{array}$$

α-Phenyl-δ-phenoxybutyl Cyanide.—In a 1-liter 3-necked flask, equipped with a stirrer, reflux condenser and dropping funnel were placed 39 g. (1 mole) of powdered sodamide and 400 cc. of ether. Then 118 g. (1 mole) of benzyl cyanide was added at such a rate that the ether refluxed gently.[11] When all of the nitrile had been added the solution was refluxed for four hours, after which time the flask was cooled to 0° in an ice salt mixture and 215 g. (1 mole) of phenoxypropyl bromide slowly added. After stirring for four hours at room temperature water was added and the ether layer separated. After removal of the ether the residue was fractionated. Lower boiling fractions consisting of benzyl cyanide and phenoxypropyl bromide came over first, after which 154 g. (63%) of α-phenyl-δ-phenoxybutyl cyanide, b. p. 190–195 (2 mm.), was collected as a pale yellow viscous liquid; d_{25}^{25} 1.0876; n_D^{25} 1.5704.

Anal. Calcd. for $C_{17}H_{17}ON$: N, 5.58. Found: N, 5.56.

β-Phenyl-ε-phenoxyamylamine Hydrochloride.—A solution of 40 g. of α-phenyl-δ-phenoxybutyl cyanide in 100 cc. of acetic anhydride was reduced catalytically over 0.5 g. of Adams platinum oxide catalyst.[12] After the reduction was complete the excess acetic anhydride was removed under diminished pressure. A thick sirup, which could not be caused to crystallize, remained. A 2-g. sample of this sirup when refluxed for thirty-six hours with 50 cc. of 20% hydrochloric acid gave, on cooling, the hydrochloride of β-phenyl-ε-phenoxyamylamine, m. p. 127–128°.

Anal. Calcd. for $C_{17}H_{22}ONCl$: C, 69.93; H, 7.62. Found: C, 69.63; H, 7.68.

3-Phenylpiperidine.—The remainder of the sirup which was obtained from the reduction of the nitrile in acetic anhydride solution was refluxed for thirty-six hours with 200 cc. of 48% hydrobromic acid and the resulting solution evaporated to dryness. The dry residue was decomposed with 5% sodium hydroxide solution and the amine layer extracted with 400 cc. of toluene. This toluene solution was separated and treated with 100 cc. of 10% sodium hydroxide solution and the mixture refluxed for four hours. The toluene layer was then distilled. A 10-g. fraction boiling at 250–260° (740 mm.) was collected as 3-phenylpiperidine. This impure product was purified by conversion into the hydrochloride and recrystallization of the latter from an alcohol–ether mixture. From the purified hydrochloride the free base was obtained by treatment with alkali.

The properties of the various phenyl and phenylalkylpiperidines which were prepared in this work together with the analyses of the new compounds are summarized in Table II.

The melting points and analyses of the hydrochlorides of the new piperidines listed in Table II are given in Table III.

Phenyl and Phenylalkyl Piperidinopropyl Benzoate Hydrochlorides.—A mixture of two moles of the substituted piperidine and one mole of γ-chloropropyl benzoate was heated at 100° until the reaction was at least 80% complete as shown by the amount of the hydrochloride of the secondary amine which precipitated when the reaction mix-

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(11) *Cf.* Bodroux and Taboury, *Bull. soc. chim.*, [4] **7**, 666 (1910); Knowles and Cloke, THIS JOURNAL, **54**, 2032 (1932).

(12) *Cf.* Carothers and Jones, *ibid.*, **47**, 3051 (1925).

TABLE II

CERTAIN PHENYL AND PHENYLALKYL SUBSTITUTED PIPERIDINES

Substituent	B. p., °C. (mm.)	d_{25}^{25}	n_D^{25}	Formula	Analyses, N, % Calcd.	Found
2-Phenyl[a]	108–110 (9)	....	....	.....	..	..
2-(γ-Phenylpropyl)	161–163 (10)	0.9721	1.5189	$C_{14}H_{21}N$	6.89	6.99
2-(δ-Phenylbutyl)	164–166 (9)	0.9575	1.5152	$C_{15}H_{23}N$	6.46	6.50
3-Phenyl	255–256 (740)	1.0040	1.5473	$C_{11}H_{15}N$	8.69	8.98
3-Benzyl[b]	279–281 (740)	....	....	.....	..	..
4-Phenyl[c]	255–258 (730)	....	....	.....	..	..

[a] *Cf.* Gabriel, *Ber.*, **41**, 2012 (1908). [b] Chloroplatinate decomposes at 191°. *Cf.* Tschitschibabin, *ibid.*, **36**, 2711 (1903). [c] M. p. 58°. Chloroplatinate melts at 205°. *Cf.* Bally, *ibid.*, **20**, 2590 (1887).

TABLE III

HYDROCHLORIDES OF SUBSTITUTED PIPERIDINES

Substituent	M. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2-(γ-Phenylpropyl)	139–141	$C_{14}H_{22}NCl$	70.11	9.25	69.80	9.30
2-(δ-Phenylbutyl)	129–131	$C_{15}H_{24}NCl$	70.96	9.53	70.87	9.69
3-Phenyl	146–147	$C_{11}H_{16}NCl$	66.80	8.16	66.87	8.23

ture was diluted with ether. After removal of this hydrochloride the ether solution of the tertiary amine was treated with dry hydrogen chloride and the precipitate purified by recrystallization from an alcohol–ether mixture. The melting points and analyses of the various substituted piperidinopropyl benzoate hydrochlorides are summarized in Table IV.

TABLE IV

PHENYL AND PHENYLALKYLPIPERIDINOPROPYL BENZOATE HYDROCHLORIDES

Substituent	M. p., °C.	Formula	Analyses, % Cl Calcd.	Found
2-Phenyl	186–187	$C_{21}H_{26}O_2NCl$	9.86	9.93
2-(γ-Phenylpropyl)	103–105	$C_{24}H_{32}O_2NCl$	8.82	8.68
2-(δ-Phenylbutyl)	179–181	$C_{25}H_{34}O_2NCl$	8.51	8.56
3-Phenyl	180–181	$C_{21}H_{26}O_2NCl$	9.86	10.07
3-Benzyl	163–164	$C_{22}H_{28}O_2NCl$	9.49	9.48
4-Phenyl	174–175	$C_{21}H_{26}O_2NCl$	9.86	9.96

Pharmacological Report.—The piperidinopropyl benzoate hydrochlorides which have been described in this paper are being studied pharmacologically by Mr. Charles L. Rose of the Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana. A preliminary report on some of their pharmacological properties is summarized in Table V. Anesthetic efficiencies were determined by application of 1% solutions of the hydrochlorides to the rabbit's cornea and noting the duration of anesthesia. Toxicities were determined by intravenous injection into white rats. The values given are, in each case, the average of a representative number of pharmacological tests.

The various anesthetics are listed by the substituent in the piperidine nucleus. For comparison the corresponding pharmacological values for the previously reported compounds containing a 2-benzyl (No. 7), a 2-phenylethyl (No. 8) and a 4-phenylethyl (No. 9) substituent are included in the table.

TABLE V

PHARMACOLOGICAL PROPERTIES OF PHENYL AND PHENYLALKYL SUBSTITUTED PIPERIDINOPROPYL BENZOATES

No.	Substituent	Duration of corneal anesthesia, minutes	Intravenous toxicity to white rats, M. L. D., mg./kg.
1	2-Phenyl	15	26
2	2-(γ-Phenylpropyl)	45	30
3	2-(δ-Phenylbutyl)	37	28
4	3-Phenyl	26	42
5	3-Benzyl	31	35
6	4-Phenyl	26	26
7	2-Benzyl	5–6 days (2% soln.)	15
8	2-(β-Phenylethyl)	5–6 days (2% soln.) 1–2 days (1% soln.)	22
9	4-(β-Phenylethyl)	51 (2% soln.)	30

Discussion of the Pharmacological Data.—It is apparent from the data in Table V that the extremely long durations of anesthesia are associated only with those substances which contain a benzyl or phenylethyl substituent in the 2 position of the piperidine nucleus (Nos. 7 and 8). Increasing the length of the carbon chain which separates the phenyl group from the nitrogen atom to more than three carbon atoms (Nos. 2 and 3) or decreasing it to one carbon atom (No. 1) diminishes very considerably the anesthetic activity of the resulting compounds. So far as the substituents in the 2 position are concerned, maximum anesthetic activity appears to reside in those structures in which the nitrogen atom is separated from the phenyl group by two or three carbon atoms. However, a comparison of compounds 4 and 7 (2 carbons between the nitrogen atom and phenyl group) and of compounds 5, 6 and 8 (3 carbons between the nitrogen atom and phenyl group) indicates that this relationship of structure to pharmacological action does not exist when the substituent groups are transferred to the 3 and 4 positions of the piperidine nucleus.

Summary

The preparation and properties of certain new phenyl and phenylalkyl piperidines have been described. These and other similarly substituted piperidines have been condensed with γ-chloropropyl benzoate to give a series of phenyl- and phenylalkyl-piperidinopropyl benzoates. Some of the pharmacological properties of these latter compounds have been described and discussed.

MADISON, WISCONSIN

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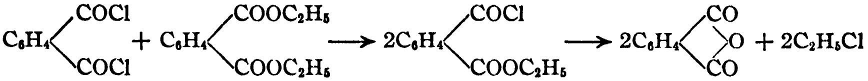
[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MONSANTO CHEMICAL COMPANY]

The Reaction between Some Acid Chlorides and Esters

BY L. P. KYRIDES AND M. N. DVORNIKOFF

In a recent paper[1] it was stated that phthalyl chloride and diethyl ether react in presence of zinc chloride to give phthalic anhydride and ethyl chloride, and not diethyl phthalate, which had been expected. It was also intimated that the diethyl phthalate, if it had been formed, must have reacted with the excess of phthalyl chloride to give the products which were isolated.

Work carried out at the same time disclosed that phthalyl chloride and dialkyl phthalates also react in presence of traces of zinc chloride to give the anhydride and the corresponding alkyl chlorides. In these reactions it appears that the ester chloride of phthalic acid is first formed, which, being very unstable, is decomposed immediately into the anhydride and the alkyl chloride as follows



$$C_6H_4\langle{}^{COCl}_{COCl} + C_6H_4\langle{}^{COOC_2H_5}_{COOC_2H_5} \longrightarrow 2C_6H_4\langle{}^{COCl}_{COOC_2H_5} \longrightarrow 2C_6H_4\langle{}^{CO}_{CO}\rangle O + 2C_2H_5Cl$$

Zelinsky[2] attempted to prepare the ester chloride of phthalic acid and observed its great instability. He states that it is decomposed even on standing in a vacuum desiccator and gives ethyl chloride and phthalic anhydride on warming.

Succinyl chloride and succinic esters react similarly, indicating that the reaction may be general with alpha-beta and *o*-dicarboxylic acids.

Senff[3] by reaction of benzoyl chloride and ethyl benzoate in the presence of zinc chloride at the boiling temperature of the mixture observed only the formation of *m*-benzoylbenzoic acid. We have found that in this case the main reaction products are benzoic anhydride and ethyl chloride. We also isolated very small amounts of anthraquinone.

The reaction of a dialkyl phthalate with benzoyl chloride or of phthalyl chloride with an alkyl benzoate results in the formation of alkyl chloride and probably of a mixture of the anhydrides of the acids as the main reaction products.

Benzyl esters in similar reactions failed to give benzyl chloride and several attempts at reaction of diethyl phthalate with aliphatic monocarboxylic acid chlorides resulted in the formation of large amounts of hydrochloric acid and ethylene. No ethyl chloride was isolated in these cases, indicating that the course of the reaction was quite different.

Experimental

1. Reaction between Dialkyl Phthalates and Phthalyl Chloride.—The reaction was carried out in a 250-cc. three-necked flask carrying a thermometer, a dropping fun-

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(1) L. P. Kyrides, THIS JOURNAL, 55, 1209 (1933).

(2) Zelinsky, *Ber.*, 20, 1010 (1887).

(3) Senff, *Ann.*, 220, 250 (1883).

nel, and a reflux spiral condenser, which was kept at the proper temperature. In the case where ethyl chloride was a reaction product the condenser was cooled with running water at 14°. In the latter case the condenser was connected through a small flask containing water (for scrubbing the gases) to a spiral condenser which was cooled with ice and water and the ethyl chloride was collected in a receiver cooled at about −5°.

Freshly distilled diethyl phthalate (166 g. (0.75 g. mole)) and 0.2 g. of technical zinc chloride were charged into the flask and heated over a gauze to 120°; 165 g. of 94% (0.764 g. mole) phthalyl chloride (containing 6% phthalic anhydride) was dropped in over a period of about three hours. Toward the end, the temperature was gradually raised to 180° and the reaction stopped when the evolution of gas ceased.

The condensate in the receiver was fractionated through a spiral condenser maintained at 14°. In this manner 88.3 g. (1.37 g. mole) of ethyl chloride was recovered. This amounts to 91% of the theoretical from diethyl phthalate. The residual phthalic anhydride, contaminated with traces of phthalyl chloride, weighed 236 g. (practically theoretical yield) and showed a crystallizing point of 128–129°. A very small amount of ethylene and some hydrochloric acid were also found to be evolved during the reaction. The reaction is, therefore, practically quantitative and follows the equation given above.

The reaction gives essentially the same yields if the components are mixed and heated very gradually to avoid too violent a reaction.

By heating di-*n*-butyl phthalate with a 10% excess of phthalyl chloride in presence of traces of zinc chloride, we obtained an 80% yield of butyl chloride. Some butylene and hydrochloric acid were also formed.

Di-*sec*-butyl phthalate and phthalyl chloride gave about 50% yield of *sec*-butyl chloride and a large amount of butylene.

Gram molecular equivalents of di-*sec*-butyl succinate and succinyl chloride were heated gradually with a trace of zinc chloride from 110–190°. The crude *sec*-butyl chloride amounted to 58% of the theoretical. At the same time 12 liters of gas (butylene) and 0.8 g. mole of hydrochloric acid were also formed.

2. Ethyl Benzoate and Benzoyl Chloride, $C_6H_5COOC_2H_5 + C_6H_5COCl = (C_6H_5CO)_2O + C_2H_5Cl$.—A mixture of equimolecular quantities of ethyl benzoate and benzoyl chloride containing about 1% by weight of technical zinc chloride was heated gradually. No appreciable reaction was apparent below 180°. The temperature was then raised slowly to 270° in the course of about two hours and maintained at 270–290° for two hours longer. The ethyl chloride obtained amounted to 77% of the theoretical. Some hydrochloric acid and ethylene were also formed. The reaction mixture was then subjected to vacuum distillation and benzoic anhydride was obtained in a 77% yield of the theoretical. The anhydride was contaminated with a very small amount of an impurity which was isolated and identified as anthraquinone.

3. Diethyl Phthalate and Benzoyl Chloride.—A mixture of 88.8 g. (0.4 g. mole) of diethyl phthalate, 112.4 g. (0.8 g. mole) of benzoyl chloride and 0.4 g. of zinc chloride was heated for one-half hour at 120–165°; 0.34 g. mole of ethyl chloride was obtained, which is equivalent to a yield of 42.5% of the theoretical. Hydrochloric acid was also formed corresponding to 0.08 mole per mole of benzoyl chloride. The reaction temperature was then raised and maintained at 180–200° for two hours longer. The yield of ethyl chloride was raised to 56%. A further heating for two hours longer increased the yield of ethyl chloride to 63%.

These results seem to indicate that the reaction proceeds in two stages. At first one mole of diethyl phthalate reacts with one of benzoyl chloride at the lower temperature giving phthalic anhydride (probably through the intermediate ester chloride of phthalic acid), ethyl benzoate and ethyl chloride. Then at the higher temperature and at a considerably slower rate, the ethyl benzoate formed reacts with another mole of benzoyl chloride as given under (2).

4. Ethyl Benzoate and Phthalyl Chloride.—This reaction was carried out as under (3) by heating 2 moles of ethyl benzoate with one of phthalyl chloride. The reaction started at about 180° and after heating at 180–200° for two hours gave a 65% yield of ethyl chloride.

Summary

Equimolecular amounts of phthalyl chloride and diethyl phthalate react in presence of traces of zinc chloride to give excellent yields of phthalic anhydride and ethyl chloride. Other alkyl esters of phthalic acid react similarly, except that the yields of the alkyl chlorides are lower due to the formation of larger amounts of alkylenes. Succinic esters and succinyl chloride react in the same manner.

Ethyl benzoate and benzoyl chloride react in the presence of zinc chloride at higher temperatures to give fair yields of benzoic anhydride and ethyl chloride.

Benzoyl chloride and phthalic esters react to give alkyl chlorides and presumably a mixture of the anhydrides of the acids as the main reaction products. The same is also true of the reaction of phthalyl chloride with ethyl benzoate.

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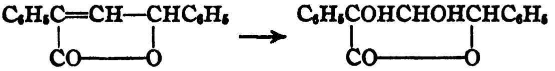
Hydroxyl Derivatives of Alpha,Gamma-Diphenylbutyric Acid

BY E. P. KOHLER AND R. H. KIMBALL

The work herein described began many years ago with an attempt to add nitromethane to phenyl benzoyl ethylene oxide in the hope of finding an explanation for the peculiar behavior of certain aliphatic nitro compounds.[1] Addition appeared to occur readily enough but experiments carried out under the most diverse conditions invariably ended with an intractable oil from which no substance containing nitrogen could be isolated. By digestion with hydrochloric acid this oil was in part converted into a solid in which all that remained of the nitromethane was an atom of carbon and possibly one or two atoms of oxygen.

From a series of transformations which need not be discussed here we came to the conclusion that the nitrogen-free solid was a dihydroxy lactone. This conclusion has been confirmed by a synthesis of the substance that adequately establishes its structure



$$\underset{\mathrm{CO}\text{————}\mathrm{O}}{C_6H_5C{=}CH{-}CHC_6H_5} \longrightarrow \underset{\mathrm{CO}\text{————}\mathrm{O}}{C_6H_5COHCHOHCHC_6H_5}$$

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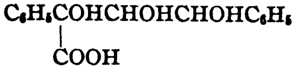
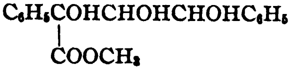
[1] Kohler and Goodwin, THIS JOURNAL, 49, 219 (1927).

Our solid product, therefore, is the gamma lactone of an α,β,γ-trihydroxy acid. Since comparatively few substances of this type are known we have studied it with some care. By well-known methods it was easily converted into the trihydroxy acid, its methyl ester and the methyl ester of the corresponding gamma chloro acid; all of these substances thus became available for comparison



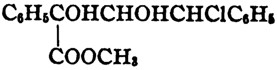
$\underset{\mathrm{COOH}}{\mathrm{C_6H_5COH}}\mathrm{CHOHCHOHC_6H_5}$

II



$\underset{\mathrm{COOCH_3}}{\mathrm{C_6H_5COH}}\mathrm{CHOHCHOHC_6H_5}$

III



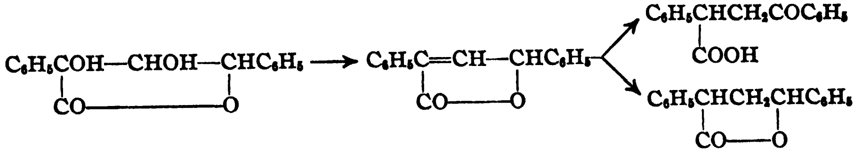
$\underset{\mathrm{COOCH_3}}{\mathrm{C_6H_5COH}}\mathrm{CHOHCHClC_6H_5}$

IV

The oxidation of these substances yielded no results of general interest. In acid media the lactone is oxidized less readily than its primary oxidation products, consequently when oxidation occurs at all it always ends in carbon dioxide and benzoic acid. In alkaline solution the salts of the trihydroxy acid reduce permanganate with great rapidity, being oxidized to benzoic and phenylglyoxylic acids.

The reduction of the lactone was studied with greater care in an attempt to secure the corresponding diphenyl tetrose. Fischer and Stewart[2] prepared a monophenyl tetrose by reducing, with sodium amalgam in a feebly acid solution, a dihydroxy lactone which differed from ours only in that it lacked the phenyl group in the alpha position. In our case this method failed completely; all of the lactone was recovered. By the prolonged action of a large excess of sodium amalgam in aqueous methyl alcohol which was maintained at a *P*H of approximately 4, we obtained a neutral product which reduced Fehling's solution, but the quantity was too small for identification. Apparently the factors which hinder the esterification of highly substituted acids also interfere with the reduction of highly substituted lactones.

The lactone is much more readily reduced with hydrogen iodide and red phosphorus but, naturally, the reduction is not to the tetrose. The principal reduction products are phenyl benzoyl propionic acid and diphenyl butyrolactone. Evidently the dihydroxyl compound is first reduced to the unsaturated lactone, and this lactone then in part is reduced further but for the most part is opened to the ketonic acid



$$\begin{array}{l}\mathrm{C_6H_5COH{-}CHOH{-}CHC_6H_5}\\ \mathrm{CO{-}{-}{-}{-}{-}{-}{-}{-}O}\end{array} \longrightarrow \begin{array}{l}\mathrm{C_6H_5C{=}CH{-}CHC_6H_5}\\ \mathrm{CO{-}{-}{-}O}\end{array} \begin{array}{l}\nearrow \begin{array}{l}\mathrm{C_6H_5CHCH_2COC_6H_5}\\ \mathrm{COOH}\end{array}\\ \searrow \begin{array}{l}\mathrm{C_6H_5CHCH_2CHC_6H_5}\\ \mathrm{CO{-}{-}{-}O}\end{array}\end{array}$$

V

Since the reduction to an unsaturated compound here, as elsewhere, depends on the presence of hydroxyl groups on adjoining carbon atoms, it can be avoided by acylating these groups. Thus both the dibenzoate of

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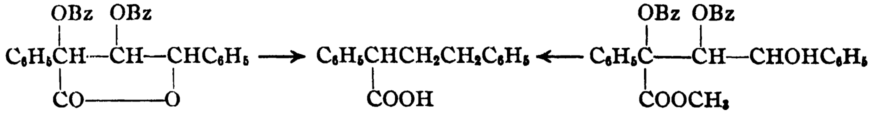
(2) Fischer and Stewart, *Ber.*, **25**, 2559 (1892).

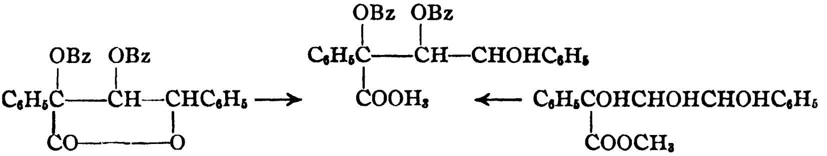
the lactone and the dibenzoate of the trihydroxy ester (III) when reduced under the same conditions pass quantitatively into diphenyl butyric acid. Here the hydroxyl groups are reduced, one by one, as they appear.



$$\begin{array}{c}\text{OBz}\quad\text{OBz}\\ |\qquad\ \ |\\ C_6H_5CH—CH—CHC_6H_5\\ |\qquad\qquad\quad |\\ CO———O\\ \text{VII}\end{array} \longrightarrow \begin{array}{c}\\ \\ C_6H_5CHCH_2CH_2C_6H_5\\ |\\ COOH\\ \text{VI}\end{array} \longleftarrow \begin{array}{c}\text{OBz}\quad\text{OBz}\\ |\qquad\ \ |\\ C_6H_5C——CH—CHOHC_6H_5\\ |\\ COOCH_3\\ \text{VIII}\end{array}$$

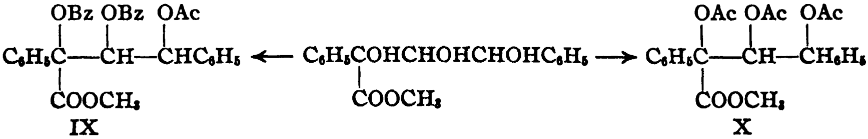
The diacetate of the lactone, which is much more easily hydrolyzed than the dibenzoate, on reduction gave a mixture composed of equal parts of phenyl benzoyl propionic and diphenylbutyric acids.

The acylation of the lactone presented no complications; boiling acetyl chloride converted it smoothly into the diacetate and benzoyl chloride in pyridine into the dibenzoate. Benzoylation of the sodium salt of the trihydroxy acid in pyridine likewise led to the dibenzoate of the lactone—doubtless because the lactone ring is closed early in the process. Benzoylation of the methyl ester of the trihydroxy acid, however, stopped with the formation of the dibenzoate of the ester. Since this same dibenzoate is formed also by the action of methyl alcoholic hydrochloric acid on the dibenzoate of the lactone, presumably the same hydroxyl groups are benzoylated in both cases



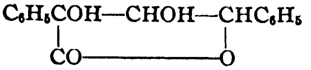
$$\begin{array}{c}\text{OBz}\quad\text{OBz}\\ |\qquad\ \ |\\ C_6H_5C——CH—CHC_6H_5\\ |\qquad\qquad\quad |\\ CO———O\end{array} \longrightarrow \begin{array}{c}\text{OBz}\quad\text{OBz}\\ |\qquad\ \ |\\ C_6H_5C——CH—CHOHC_6H_5\\ |\\ COOH_3\end{array} \longleftarrow \begin{array}{c}\\ \\ C_6H_5COHCHOHCHOHC_6H_5\\ |\\ COOCH_3\end{array}$$

The dibenzoate of the ester does not, however, like the trihydroxy ester itself, lose methyl alcohol and form the lactone when it is heated. It is possible, therefore, that the prolonged action of methyl alcoholic hydrogen chloride causes a shift of one of the benzoyl groups—hence the structure of the benzoylated ester cannot be regarded as certain. Although the third hydroxyl group of the ester cannot be benzoylated it can be acetylated; the resulting triacyl derivatives supply the final proof of the presence of all three hydroxyl groups:

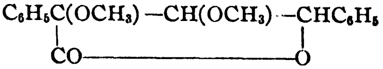


$$\begin{array}{c}\text{OBz}\ \text{OBz}\ \text{OAc}\\ |\qquad |\qquad |\\ C_6H_5C——CH—CHC_6H_5\\ |\\ COOCH_3\\ \text{IX}\end{array} \longleftarrow \begin{array}{c}\\ \\ C_6H_5COHCHOHCHOHC_6H_5\\ |\\ COOCH_3\\ \\ \end{array} \longrightarrow \begin{array}{c}\text{OAc}\ \text{OAc}\ \text{OAc}\\ |\qquad |\qquad |\\ C_6H_5C——CH—CH_6H_5\\ |\\ COOCH_3\\ \text{X}\end{array}$$

The methylation of the lactone likewise presented no complications. Depending upon the temperature and the amount of methylating agents employed, it gave either a mixture of two monomethyl derivatives or the completely methylated lactone. Each of the monomethyl derivatives is converted into the same dimethyl derivative by further methylation; these substances are therefore structural isomers. An attempt to determine which of them is the alpha and which the beta methoxyl compound by oxidation was unsuccessful because each of them was oxidized to a mixture of benzoic and phenylglyoxylic acids.

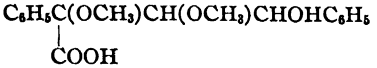


$$\begin{array}{l}C_6H_5\underset{|}{C}OH\text{—}CHOH\text{—}\underset{|}{C}HC_6H_5\\ CO\text{————}O\end{array}$$



$$\begin{array}{l}C_6H_5\underset{|}{C}(OCH_3)\text{—}CH(OCH_3)\text{—}\underset{|}{C}HC_6H_5\\ CO\text{——————}O\end{array}$$

XI



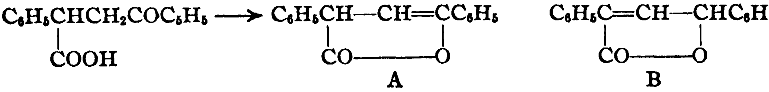
$$\begin{array}{l}C_6H_5\underset{|}{C}(OCH_3)CH(OCH_3)CHOHC_6H_5\\ COOH\end{array}$$

XII

Methylation of the trihydroxy acid gave results which are more difficult to interpret. Here the principal product is a mono methylated acid in which the methoxyl group is in the gamma position. Accompanying this acid are small quantities of the alpha or beta methoxy acid corresponding to the higher melting monomethylated lactone, the α,β-dimethoxy acid XII and another dimethylated acid in which one of the methoxyl groups is in the gamma position. The completely methylated acid could not be obtained. More than 70% of the product has methoxyl in the gamma position and more than 66% in this position alone—a result which could not have been anticipated either from the relative acidity of the hydroxyl groups or from the space relations.

Experimental Part

Dihydroxy diphenylbutyro lactone is now most easily made from phenyl benzoyl propionic acid. A long time ago Anschütz and Montfort[3] found that when this acid is heated with acetic anhydride it loses water and forms a diphenyl crotonic lactone. In view of the method of formation they naturally assumed that the lactone was unsaturated in the β,γ-position and consequently represented it with formula A.



$$\begin{array}{l}C_6H_5\underset{|}{C}HCH_2COC_6H_5\\ COOH\end{array} \longrightarrow \begin{array}{l}C_6H_5\underset{|}{C}H\text{—}CH{=}\underset{|}{C}C_6H_5\\ CO\text{———}O\end{array} \qquad \begin{array}{l}C_6H_5C{=}\underset{|}{C}H\text{—}\underset{|}{C}HC_6H_5\\ CO\text{———}O\end{array}$$

A B

Some years later Thiele[4] after an extensive study of unsaturated gamma lactones decided that in most of them the double linkage was in the α,β-position. Thiele also showed that it is possible to distinguish between the two types of unsaturated lactones by oxidation with permanganate because only those which have the double linkage in the α,β-position can be oxidized to dihydroxy lactones. In view of Thiele's work it seemed probable to us that the lactone prepared by Anschütz and Montfort should be represented by formula B and that consequently it should be oxidizable to

[3] Anschütz and Montfort, *Ann.*, **284**, 3 (1895).

[4] Thiele and Wedemann, *ibid.*, **347**, 132 (1906).

dihydroxy diphenylbutyro lactone. We have found that it is oxidizable and that the yield of dihydroxyl compound is excellent. Our procedure is as follows.

In a 4-liter bottle, provided with an efficient mechanical stirrer and surrounded with a freezing mixture, is placed a solution of 60 g. of the unsaturated lactone in 750 cc. of acetone and 10 cc. of water. Into this solution is stirred first 25 g. of very finely powdered anhydrous magnesium sulfate, then a well-cooled solution of 50 g. of potassium permanganate in 300 cc. of water and 1700 cc. of acetone. The permanganate is added as fast as possible without raising the temperature above −4°. Oxidation is rapid and the reaction is complete in an hour. Excess of permanganate is removed by adding bisulfite and acid until the solution clears. The oxides of manganese are then collected on a filter, washed well with acetone and discarded.

The filtrate is distilled to about 750 cc. then gradually diluted to 2 liters with water and cooled in a freezing mixture. It deposits 38–40 g. of practically pure dihydroxy lactone melting at 145–146°. The pure lactone, obtained by recrystallization from aqueous acetic acid, melts at 149°.

Anal. Calcd. for $C_{16}H_{14}O_4$: mol. wt., 270; C, 71.1; H, 5.2. Found: mol. wt., 262; C, 71.1; H, 5.3.

The lactone is readily soluble in ether, alcohol and acetone; moderately soluble in hot water and in benzene. It crystallizes well from benzene and from dilute acetic acid in colorless prisms.

α,γ-Diphenyl-α,β,γ-trihydroxybutyric Acid II.—The pure sodium salt of the trihydroxy acid was prepared by dissolving the lactone in excess of hot sodium carbonate, evaporating the solution to dryness, and extracting the organic sodium salt from the residue with absolute ethyl alcohol. It crystallized from the alcoholic solution in needles containing a molecule of alcohol.

Anal. Calcd. for $C_{16}H_{15}O_5Na \cdot C_2H_5OH$: C_2H_5OH, 12.9. Found: loss at 105°, 13.2. Calcd. for $C_{16}H_{15}O_5Na$: Na, 7.4. Found: Na, 7.4.

When a mineral acid is added to an aqueous solution of the sodium salt it produces an amorphous precipitate which is probably a hydrated form of the trihydroxy acid. The precipitate is sparingly soluble in nearly all organic solvents. It melts at 150–157°, loses water with effervescence, and passes into the lactone. The crystalline acid was obtained but once by concentrating and cooling an ethereal solution. It separated in needles which melted with loss of water at 151°.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.7; H, 5.5. Found: C, 66.2; H, 5.6.

The methyl ester (III) of the trihydroxy acid was made by means of the silver salt which was obtained from the sodium salt in the usual manner. After it had been washed with absolute alcohol and dried *in vacuo* it was found to be anhydrous.

Anal. Calcd. for $C_{16}H_{15}O_5Ag$: Ag, 27.3. Found: Ag, 27.2.

A suspension of the dry silver salt in absolute ether containing excess of methyl iodide was left to itself overnight, then boiled for several hours, and finally evaporated to dryness under diminished pressure. From the residue the ester was extracted with boiling benzene, from which it crystallized well on cooling, and it was finally purified by recrystallization from ethyl acetate and petroleum ether. The yield was 14.6 g. from 20 g. of the silver salt.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.6; H, 6.0; active H, 3.0. Found: C, 67.4; H, 6.1; active H, 3.0.

The ester crystallized in fine colorless needles. Owing to the ease with which it loses methyl alcohol, it has no true melting point. In a capillary tube it softens at about

115°, liquefies with frothing at about 125°, then resolidifies and finally melts at the same temperature as the lactone.

Methyl α,γ-Diphenyl-α,β-dihydroxy-γ-chlorobutyrate, IV.—A solution of 6 g. of the lactone in 50 cc. of dry methyl alcohol was saturated with dry hydrogen chloride, left to itself for forty-eight hours, then poured into ice water. The product crystallized from ether–petroleum ether in fluffy needles melting at 124°. An analysis proved that but one hydroxyl group is replaced by chlorine, and the ease with which the lactone was regenerated from the chloro ester showed that the chlorine is in the gamma position.

Anal. Calcd. for $C_{17}H_{17}O_4Cl$: C, 63.8; H, 5.3. Found: C, 63.4; H, 5.3.

Reduction.—The unsuccessful attempts to reduce the lactone to diphenyltetrose that were discussed in the introduction need not be described in detail. The reduction with hydrogen iodide was carried out as follows. A mixture of 2 g. of lactone, 0.8 g. of red phosphorus and 12 g. of 45% hydriodic acid in glacial acetic acid was boiled for fifteen hours, then filtered and greatly diluted with water. The water solution, manipulated in the usual manner, yielded 1.0 g. of pure phenyl benzoyl propionic acid and 0.2 g. of α,γ-diphenylbutyro lactone (V) which melted at 103–104.5° and which was identified by comparison with an authentic sample.

When the dibenzoate of the lactone was reduced in the same manner the principal product was an acid which crystallized from petroleum ether in prisms and which melted at 75°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 79.9; H, 6.8.

Since the composition of the acid indicated complete reduction to diphenyl butyric acid we undertook the preparation of this acid by a Clemmensen reduction. To this end we boiled 10 g. of phenyl benzoyl propionic acid and 100 g. of amalgamated zinc with concentrated hydrochloric acid for fifteen hours during which time a total of 130 cc. of hydrochloric acid was added in steps. From the product we isolated 6.9 g. of the same acid that had been obtained from the dibenzoate.

Acetylation.—The general methods employed in acetylating and benzoylating both the lactone and the methyl ester of the trihydroxy acid have been adequately indicated in the introduction. The products were recrystallized either from methyl alcohol or from ether–petroleum ether. Their composition and properties are shown in the table.

Formulas				Composition					
				Calculated, %			Found, %		
Empirical	Structural	Crystal form	M. p., °C.	C	H	OCH_3	C	H	OCH_3
$C_{20}H_{18}O_6$	VII[a]	Rhombic plates	135	67.8	5.1		67.3	5.2	
$C_{18}H_{16}O_5$	VII[b]	Prisms	138	69.2	5.2		69.0	5.2	
$C_{30}H_{22}O_6$	VII	Prisms	144	75.3	4.6		75.4	4.6	
$C_{31}H_{26}O_7$	VIII	Plates	178	72.9	5.1	6.1	72.5	5.1	5.7
$C_{33}H_{28}O_8$	IX	Prisms	157	71.7	5.1	5.6	71.4	5.1	5.4
$C_{23}H_{24}O_8$	X	Prisms	153	64.5	5.6	7.2	64.2	5.6	7.1

[a] Diacetate of the lactone. [b] Monoacetate of the lactone.

Methylation: α,γ-Diphenyl-α,β-dimethoxybutyro Lactone (XI).—For the purpose of complete methylation a mixture composed of a solution of 10.8 g. of the lactone in 25 cc. of absolute methyl alcohol, 49.7 g. of silver carbonate and 56.8 g. of methyl iodide was boiled under an excess pressure of approximately half an atmosphere. Evolution of carbon dioxide was brisk at first, but soon became slow and regular. After fourteen hours the solvent was evaporated and the residue extracted with boiling methyl alcohol. The resulting solution on evaporation and cooling yielded 6.34 g. of solid and 5.0 g. of a viscous oil. On re-methylation in the same manner, the oil yielded an additional 4.07 g. of solid, making the total 87.3%.

The dimethylated lactone is readily soluble in nearly all common organic solvents. It was purified by recrystallization from methyl alcohol from which it separated in stout prisms melting at 118° and subliming slowly at 100°.

Anal. Calcd. for $C_{16}H_{12}O_2(OCH_3)_2$: OCH_3, 20.8. Found: OCH_3, 20.7.

With a view to partial methylation a similar but more dilute mixture of lactone, methyl alcohol, methyl iodide and silver carbonate was left to itself at the ordinary temperature for forty-three hours, then treated as in the preceding experiment. The proportion of dimethylated lactone was much less and some unmethylated lactone was recovered. By a somewhat laborious fractional crystallization from carbon tetrachloride the residual oil was separated into two isomeric monomethylated lactones, melting, respectively, at 143 and 77°.

The higher melting isomer is sparingly soluble in carbon tetrachloride and much less soluble than the dihydroxy lactone in water or dilute acetic acid. It crystallizes in minute prisms. Like the dimethylated lactone it is practically insoluble in cold aqueous alkalies but is readily soluble in aqueous alcoholic carbonates.

Anal. Calcd. for $C_{16}H_{13}O_3OCH_3$: OCH_3, 10.9. Found: OCH_3, 10.8.

The lower melting isomer is dimorphous. It first crystallized in large lustrous prisms melting at 77°. Later a less soluble form appeared which crystallized in small thin plates and melted at 112°. Once this form had made its appearance it was the only one that could be isolated.

Anal. Calcd. for $C_{16}H_{13}O_3OCH_3$: OCH_3, 10.9. Found: (77°) OCH_3, 10.8; (112°) OCH_3, 10.5.

The relative amounts in which the products were obtained are as follows: unchanged dihydroxy lactone, 13%; dimethylated lactone 22%; monomethylated lactones (112°) 34%, (143°) 14%.

α,β-Dimethoxy-γ-hydroxybutyric Acid (XII).—The methylated lactone is scarcely affected by cold aqueous alkaline hydroxides but is readily soluble in alcoholic hydroxides and in aqueous alcoholic carbonates. The resulting potassium salt, being sparingly soluble in excess carbonate, is readily obtained in a pure condition. It crystallizes from aqueous acetone in needles containing water of crystallization.

Anal. Calcd. for $C_{18}H_{19}O_5K \cdot 1.5H_2O$: H_2O, 7.1; OCH_3, 16.3. Found: H_2O, 7.0; OCH_3, 16.1.

The corresponding acid was purified by recrystallization from ethyl acetate, in which it is far less soluble than the dimethylated lactone. It separated in fine needles melting with decomposition at 129°. After one crystallization from aqueous methyl alcohol about half of it had been converted to the lactone.

Anal. Calcd. for $C_{18}H_{20}O_5$: OCH_3, 19.6. Found: OCH_3, 19.5.

Methylation of the Trihydroxy Acid: α,γ-Diphenyl-α,β-dihydroxy-γ-methoxybutyric Acid.—To a solution of 5.4 g. of the dihydroxy lactone in 60 cc. of 20% sodium hydroxide was added drop by drop, with vigorous mechanical stirring, 16 g. of dimethyl sulfate, while the temperature was held at 35°. After half an hour, when all the sulfate had disappeared, the addition of the same quantities of sulfate and hydroxide was repeated. Stirring was continued for several hours with addition of sufficient water to keep sparingly soluble salts in solution. The mixture was then made strongly acid, heated for the purpose of converting any hydroxy acids into lactones, and separated into neutral and acid products in the usual manner.

The neutral products were small quantities of the monomethoxy lactone melting at 143° and the dimethoxy lactone. The acid fraction was composed largely of two substances which were most readily separated by treatment with cold chloroform. The residue, insoluble in chloroform, on recrystallization from aqueous methyl alcohol yielded 3.25 g. of the γ-methoxy acid melting at 201° and crystallizing in small rhombic plates.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.5; H, 6.0; OCH_3, 10.3. Found: C, 67.6; H, 6.3; OCH_3, 10.0

The chloroform solution, on suitable treatment, yielded 0.18 g. of a dimethoxy acid which by recrystallization from very dilute alcohol was obtained in fine needles melting at 148–149°.

Anal. Calcd. for $C_{18}H_{20}O_5$: C, 68.3; H, 6.4; OCH_3, 19.6. Found: C, 68.2; H, 6.5; OCH_3, 19.0.

This same dimethoxy acid was obtained by intensive methylation of the gamma methoxy acid, but the yield was exceedingly small.

Summary

This paper contains a description of the preparation, oxidation, reduction, alkylation and acylation of α,γ-diphenyl dihydroxy butyro lactone.

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Chloro Derivatives of Benzyl Phenols. II. Some Monochloro, Dichloro and Trichloro Derivatives of Ortho and Para Benzyl Phenols

BY R. C. HUSTON, R. L. GUILE, P. S. CHEN, W. N. HEADLEY, G. W. WARREN, L. S. BAUR AND B. O. MATE

Continuing our studies on the benzylation of phenols, we have prepared chloro derivatives of ortho and para benzylphenols. A number of the dichloro derivatives of ortho and para benzylphenols have been described in an earlier article from this Laboratory.[1]

Condensations by means of aluminum chloride were carried out according to the technique previously described.[1,2] The mole proportions of reactants used were: one of benzyl chloride (or alcohol), three of phenol and one-half of aluminum chloride except in cases where 2,6-dichlorophenol was a reactant when the phenol and benzyl chloride were used in the ratio of one to one.

Temperatures between 20 and 35° were found to be satisfactory. In some cases with 2,6-dichlorophenol condensation failed to take place at lower temperatures.

In all cases the distillate from the ether extract was examined for benzyl ethers by dissolving in Claisen's alcoholic potash[3] and extracting with petroleum ether. The phenols were then liberated by treatment with hydrochloric acid and again extracted with ether.

(1) Huston and Eldridge, THIS JOURNAL, **53**, 2260 (1931).

(2) Huston and others, *ibid*, **46**, 2775 (1924); **49**, 1366 (1927); **52**, 448 (1930); **53**, 2379 (1931); **54**, 1506 (1932).

(3) Claisen, *Ann.*, **442**, 224 (1924).

Condensations with Benzyl Alcohol (or Chloride).—Benzyl alcohol (or chloride) with 2-chlorophenol, by the aluminum chloride method, gave 4-hydroxy-3-chlorodiphenylmethane and 2-hydroxy-3-chlorodiphenylmethane.

The benzylation of 2-chlorophenol by the Claisen method[4] gave 2-hydroxy-3-chlorodiphenylmethane and 2-chlorophenyl benzyl ether. When 2-hydroxy-3-chlorodiphenylmethane and 4-hydroxy-3-chlorodiphenylmethane[5] were chlorinated in chloroform solution, they yielded 2-hydroxy-3,5-dichlorodiphenylmethane and 4-hydroxy-3,5-dichlorodiphenylmethane,[1] respectively.

The benzylation by the Claisen method of 4-chlorophenol yielded 2-hydroxy-5-chlorodiphenylmethane and 4-chlorophenyl benzyl ether while further attempts to benzylate the 2-hydroxy-5-chlorodiphenylmethane resulted in the formation of 4-chloro-2-benzylphenyl benzyl ether. Direct chlorination of 2-hydroxy-5-chlorodiphenylmethane gave 2-hydroxy-3,5-dichlorodiphenylmethane.[1] Benzylation by aluminum chloride of 4-chlorophenol gave 2-hydroxy-5-chlorodiphenylmethane.

Condensation with Chlorobenzyl Chloride.—Phenol was condensed with 2-chlorobenzyl chloride, 3-chlorobenzyl chloride and 4-chlorobenzyl chloride by the Claisen and aluminum chloride methods.

As a means of determining the structure of the compounds prepared, condensations of each of the chloro substituted benzyl chlorides were made with 2,4-dichlorophenol by the Claisen method and with 2,6-dichlorophenol by the aluminum chloride method. The trichlorobenzylphenols obtained by these condensations were then prepared by the cold chlorination of the corresponding monochlorobenzylphenols in chloroform. In no case was it possible to introduce chlorine into the benzyl nucleus, the chlorine entering only in the unoccupied ortho or para positions in the phenolic ring.

Claisen Method.—Phenol with 2-chlorobenzyl chloride in toluene yielded 2 hydroxy-2′-chlorodiphenylmethane and 2-chlorobenzyl phenyl ether; phenol with 3-chlorobenzyl chloride yielded 2-hydroxy-3′-chlorodiphenylmethane and 3-chlorobenzyl phenyl ether; phenol with 4-chlorobenzyl chloride yielded 2-hydroxy-4-chlorodiphenylmethane and 4-chlorobenzyl phenyl ether.

The treatment of 2,4-dichlorophenol in toluene with 2-chlorobenzyl chloride gave 2-hydroxy-3,5,2′-trichlorodiphenylmethane and 2-chlorobenzyl 2,4-chlorophenyl ether; 2,4-dichlorophenol and 3-chlorobenzyl chloride yielded 2-hydroxy-3,5,3′-trichlorodiphenylmethane and 3-chlorobenzyl 2,4-dichlorophenyl ether; 2,4-dichlorophenol with 4-chlorobenzyl chloride yielded 2-hydroxy-3,5,4′-trichlorodiphenylmethane and 4-chlorobenzyl 2,4-dichlorophenyl ether.

Aluminum Chloride Method.—Phenol with 2-chlorobenzyl chloride yielded 4-hydroxy-2′-chlorodiphenylmethane and 2-hydroxy-2′-chlorodiphenylmethane; phenol with 3-chlorobenzyl chloride yielded 4-hydroxy-3′-chlorodiphenylmethane; phenol with 4-chlorobenzyl chloride yielded 4-hydroxy-4′-chlorodiphenylmethane.

The condensation of 2,6-dichlorophenol with 2-chlorobenzyl chloride yielded 4-hydroxy-3,5,2′-trichlorodiphenylmethane; with 3-chlorobenzyl chloride it yielded 4-hydroxy-3,5,3′-trichlorodiphenylmethane; and with 4-chlorobenzyl chloride, 4-hydroxy-3,5,4′-trichlorodiphenylmethane.

In no case was the chlorobenzyl ether of any of the above phenols obtained in the aluminum chloride condensations. It will be observed that an ortho substituted product was produced along with the para benzylated phenol in the aluminum chloride condensation of phenol and 2-chlorobenzyl chloride. We were not able to isolate ortho substitution products in either the condensation of phenol with 3-chlorobenzyl chloride or phenol with 4-chlorobenzyl chloride. In the first case the boiling points of 2-hydroxy-3′-chlorodiphenylmethane and 4-hydroxy-3′-chlorodiphenylmethane did not differ enough

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(4) Claisen, *Ann.*, **442**, 221 (1924).

(5) Peratoner, *Gazz. chim. ital.*, **28**, I, 197–240 (1898).

to permit efficient separation by fractional distillation. (A rather low initial melting point of the esters of 4-hydroxy-3′-chlorodiphenylmethane would indicate the formation of a small amount of the ortho isomer.) In the second case, there was apparently none formed for both 2-hydroxy-4′- and 4-hydroxydiphenylmethane were solid crystalline substances which were definitely isolable.

Condensations in Methyl Alcohol.—The 2-chlorobenzyl phenyl ether, 3-chlorobenzyl phenyl ether and 4-chlorobenzyl phenyl ether were prepared by heating phenol and the various monochlorobenzyl chlorides in the presence of sodium methylate in methyl alcohol. Similarly, 2-chlorobenzyl 2,4-dichlorophenyl ether, 3-chlorobenzyl 2,4-dichlorophenyl ether and 4-chlorobenzyl 2,4-dichlorophenyl ether were prepared by the condensation of 2,4-dichlorophenol with 2-chlorobenzyl chloride, 3-chlorobenzyl chloride and 4-chlorobenzyl chloride, respectively.

These ethers were found to be identical with those obtained in the Claisen condensation.

Comparison of Yields.—In the Claisen condensations the yields of the benzylated phenols arranged in the order of descending magnitude were 2-hydroxy-5-chlorodiphenylmethane 43.4%, 2-hydroxy-3-chlorodiphenylmethane 27%, 2-hydroxy-4′-chlorodiphenylmethane 25%, 2-hydroxy-2′-chlorodiphenylmethane 16.71% and 2-hydroxy-3′-chlorodiphenylmethane 7.78%. In the case of the 2-hydroxy-3′-chlorodiphenylmethane the yield was increased about five-fold by adding 30 g. of 3-chlorobenzyl chloride to the reaction mixture of half mole quantities. These yields were in the order expected from consideration of the hydrolysis rates[6] of these and analogous bromine compounds and the yields from the corresponding bromobenzyl chlorides.[7]

The 4-hydroxy-2′-chlorodiphenylmethane, 4-hydroxy-4′-chlorodiphenylmethane and 4-hydroxy-3′-chlorodiphenylmethane obtained from aluminum chloride condensations were obtained in yields of 14.74, 15.84 and 46%, respectively.

The yields where given of the trichloro derivatives formed by condensing the various chlorobenzyl chlorides with 2,4-dichlorophenol by the Claisen method and with 2,6-dichlorophenol by the aluminum chloride reaction appear to be in the same order but less than in the condensations with unsubstituted phenol. This fact points to a decrease in activity where the phenolic ring is substituted with chlorine.

TABLE I

CHLORO DERIVATIVES OF BENZYLPHENOLS

Compound Chlorodiphenylmethane	Crystalline structure	M. p., °C.	Yield, %	Chlorine, % Found	Chlorine, % Calcd.
2-Hydroxy-2′-	Light green oil. On standing, pink	B. p. 146–151 (3 mm.)	16.21	16.88	16.22
2-Hydroxy-3-	White soft needles from pet. ether	40.5–41.5	27	15.89	16.22
2-Hydroxy-3′-	Brownish oil	B. p. 192–194(14 mm.)	7.78	16.38	16.22
2-Hydroxy-5-[8]	White needles from alc.	48–49	43.4	16.11	16.22
2-Hydroxy-4′-[8]	Needles in rosets from alc.	60–61	25	16.37	16.22
4-Hydroxy-2′-	White needles from ligroin	68–69	14.74	15.95	16.22
4-Hydroxy-3-	Oil	B. p. 145–148(3 mm.)	40	16.09	16.22
4-Hydroxy-3′-	Brownish oil	B. p. 200–202(14 mm.)	15.84	16.00	16.22
4-Hydroxy-4′-[8]	Needles in rosets from ligroin	87–87.5	46	16.06	16.22
2-Hydroxy-5,4′-di-	Oily crystals	44.5–45.5	15	25.63	26.9
2-Hydroxy-3,5,2′-tri-	Needles in rosets from alc.	59.5–60.5		36.75	37.01
2-Hydroxy-3,5,3′-tri-	Flakes from pet. ether	59.4–60	4.56	36.89	37.01
2-Hydroxy-3,5,4′-tri-	Fine needles from alc.	69.5–70.5		36.94	37.01
4-Hydroxy-3,5,2′-tri-	White needles from ligroin	86.5–87.5	16.8	36.81	37.01
4-Hydroxy-3,5,3′-tri-	Short white needles from pet. ether	79–80	11.52	36.95	37.01
4-Hydroxy-3,5,4′-	Long needles from pet. ether	61.5–62.5	35	36.99	37.01

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(6) Oliver, *Rec. trav. chim.*, **49**, 698–997 (1930).

(7) Huston and others, THIS JOURNAL, **55**, 2146 (1933).

(8) Klarmann, Gates and Shternov, *ibid.*, **54**, 3323 (1932).

TABLE II

CHLORO DERIVATIVES OF BENZYL PHENYL ETHERS

Compound Ether	Crystalline structure from alcohol	M. p., °C.	Yield, %	Chlorine, % Found	Chlorine, % Calcd.
2-Chlorobenzyl phenyl	Oil	B. p. 140–145(2.5 mm.)		15.51	16.22
3-Chlorobenzyl phenyl	Transparent plates	36–36.4	10.89	16.20	16.22
4-Chlorobenzyl phenyl	Plate-like crystals	85.5–86.5	5.8	15.84	16.22
4-Chlorobenzyl-4-chlorophenyl	Needles	80–81	3	28.01	27.83
2-Chlorobenzyl-2,4-dichlorophenyl	White needles	61–62		36.78	37.01
3-Chlorobenzyl-2,4-dichlorophenyl	Long white needles	42–42.5	1.46	37.2	37.01
4-Chlorobenzyl-2,4-dichlorophenyl	Needles from alc.	64.5–65.5	2.6	36.40	37.01
2-Chlorophenyl benzyl	Yellow oil	B. p. 138–140(3 mm.)	7.5	15.75	16.24
4-Chlorophenyl benzyl	Long white needles	70–71	7 3	15.64	16.23
4-Chloro-2-benzylphenyl benzyl	Lustrous plates	53–54	59	11.13	11.49

TABLE III

ESTERS OF THE VARIOUS PHENOL DERIVATIVES PREPARED ACCORDING TO THE METHOD OF EINHORN AND HOLLAND[9]

Benzoyl ester of chlorodiphenylmethane	Crystalline structure from alcohol	M. p., °C.	Chlorine, % Found	Chlorine, % Calcd.
2-Hydroxy-2′-	Yellow oil	B. p. 173–176(2.5 mm.)	10.81	11.00
2-Hydroxy-3-	Large oblong crystals	69–71	11.18	11.007
2-Hydroxy-3′-	White flakes	67 67.4	11.13	11.00
2-Hydroxy-5-	White needles	54–55	10.81	11.00
4-Hydroxy-2′-	White flakes	64.5–65.5	11.10	11.00
4-Hydroxy-3-	Small thin flakes	71–73	11.00	11.007
4-Hydroxy-3′-	Fine needles	57.5–58.0	10.96	11.00
4-Hydroxy-4′-	Large white needles	115–116	10.93	11.00
2-Hydroxy-5,4′-di-	Prismatic plates	84.5–85.5	19.9	19.78
2-Hydroxy-3,5,2′-tri-	Fine white needles	81–82	27.00	27.17
2-Hydroxy-3,5,3′-tri-	Fine white needles	63.5–64.0	27.14	27.17
4-Hydroxy-3,5,2′-tri-	Small white needles	86–87	27.43	27.17
4-Hydroxy-3,5,3′-tri-	Flakes in rosets	130–130.4	27.46	27.17
4-Hydroxy-3,5,4′-tri-	White flakes	116–117	26.95	27.17
Benzene sulfonyl ester of chlorodiphenylmethane				
2-Hydroxy-3-	Coarse white needles	62–64	1.92	9.902
2-Hydroxy-5-	White needles	68–69	9.63	9.902
4-Hydroxy-3-	Granular crystals	65–68	9.677	9.902
2-Hydroxy-3,5,3′-tri-	Plates in clumps	114.5–115	24.85	24.88
***p*-Toluene ester of chlorodiphenylmethane**				
2-Hydroxy-3-	Small white crystals	81.5–83.5	9.49	9.53
2-Hydroxy-5-	Flakes, white	75–75.5	9.28	9.53
4-Hydroxy-3-	Small granular	51–53	9.41	9.53
2-Hydroxy-3,5,3′-tri-	Coarse white needles	125.4–126	24.01	24.09
4-Hydroxy-3,5,3′-tri-	Coarse white needles	104.5–105	24.01	24.09

An absence of ether formation will be noted in all aluminum chloride condensations described in this paper. Since a large yield of 2,6-dichlorophenyl benzyl ether was obtained by condensing 2,6-dichlorophenol and benzyl chloride with aluminum chloride, these results were not expected. It is also worthy of note that the three monobromobenzy lchlorides[7] gave good yields of ethers when condensed under the same conditions with phenol but no ethers when condensed with bromophenols.

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(9) Einhorn and Holland, *Ann.*, **301**, 95 (1898).

These findings suggest a generalization to the effect that chlorine (unlike bromine) in the ring of benzyl chlorides is not favorable to ether formation.

Summary

Some monochloro, dichloro and trichloro derivatives of the benzylphenols and benzyl phenyl ethers were prepared.

No ethers were formed in the aluminum chloride condensations where chlorine was present in the nucleus of the benzyl chloride.

In the Claisen reaction the presence of chlorine in the nucleus of the benzyl chloride exerted a retarding influence on the yield of benzylated phenol and its corresponding ether, the greatest retarding effect being exhibited when the chlorine was in the meta position, the next when in the ortho and the least when in the para position.

The yields of the benzylated phenol by the Claisen reaction in case of meta substituted benzyl chloride was increased by adding the corresponding benzyl ether to the reaction mixture.

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Addition Reactions of Unsaturated Alpha-Ketonic Acids. III

BY MARIE REIMER AND HELEN H. KAMERLING

The reaction of bromine with benzalpyruvic acid and with its *p*-methoxy and *o*-methoxy substitution products has been described in earlier papers.[1] The reaction in every case was the same: addition of bromine to the ethylenic linkage of the side chain. The acids themselves, however, as well as their bromination products, differ in certain respects so strikingly that it seemed of value to continue the investigation of these compounds for the purpose of studying the effect of methoxyl groups in different positions in the benzene ring on the reactions of the molecule.

The present paper describes the preparation and reaction with bromine of benzalpyruvic acid in which a methoxyl group is in the meta position to the side chain. This is of interest not only for comparison with other unsaturated α-ketonic acids of this series but particularly in view of the behavior of *m*-methoxycinnamic acid on treatment with bromine. This is described by Davies and Davies[2] as substitution in the ring with no addition to the ethylenic linkage of the side chain. So unusual is this behavior of a cinnamic acid that one is justified in reading the conclusions of Davies and Davies with surprise and even with a certain measure of skepticism. We have repeated these experiments as described by Davies and Davies and also under other conditions of temperature and with several different

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(1) Reimer, THIS JOURNAL, 48, 2454 (1926); Reimer and Howard, *ibid.*, 50, 2506 (1928).

(2) Davies and Davies, *J. Chem. Soc.*, 602 (1928).

solvents. Our results substantiate those of these authors in every particular. With one molecular proportion of bromine 6-bromo-3-methoxycinnamic acid is formed in quantitative yield. With an excess of bromine a mixture of products results: 6-bromo-3-methoxy-, 4-(or 2)-6-dibromo-3-methoxycinnamic acids and substituted cinnamic acids with bromine undoubtedly also in the side chain. We have been no more successful than Davies and Davies in separating this mixture completely but we have found it possible to prepare *m*-methoxycinnamic acids with bromine in the side chain readily and in quantity from corresponding benzalpyruvic acids. *m*-Methoxybenzalpyruvic acid reacts normally with bromine, a dibromide being formed by addition at the ethylenic linkage. The unsaturated bromo acid obtained from this product by loss of hydrogen bromide gives, on oxidation with hydrogen peroxide, α-bromo-*m*-methoxycinnamic acid. On bromination of this bromocinnamic acid substitution takes place in the ring, α-bromo-6-bromo-3-methoxycinnamic acid being formed. This same compound can be prepared by bromination of β-bromo-*m*-methoxybenzalpyruvic acid and subsequent oxidation of the β-bromo-6-bromo-3-methoxybenzalpyruvic acid thus formed.

In its reaction with bromine, then, *m*-methoxybenzalpyruvic acid differs from *m*-methoxycinnamic acid but is like the other ketonic acids of this series. It most closely resembles the *o*-methoxy isomer although it is not so deeply colored nor so sensitive to reagents nor to light. Like the *o*-methoxy derivative it does not combine with solvents of crystallization, a conspicuous property of benzalpyruvic and *p*-methoxybenzalpyruvic acids; its dibromide is unstable like that of the *o*-methoxy compound and it is somewhat sensitive to light.

Experimental Part

Preparation of *m*-Methoxybenzalpyruvic Acid.—The *m*-methoxybenzaldehyde needed for this preparation was at first prepared by methylation of *m*-hydroxybenzaldehyde according to the directions of Posner.[3] As poor yields were obtained the following modification of the method used by Hodgson and Beard[4] for methylation of bromo-*m*-hydroxy benzaldehydes was used. Fifty grams of *m*-hydroxybenzaldehyde (0.24 mole) was placed in a three-necked flask fitted with return condenser and dropping funnels, a solution of 11 g. of sodium hydroxide in 250 cc. of water was added, the solution brought to the boiling point and 67 g. (0.32 mole) of dimethyl sulfate added rapidly enough to keep the solution boiling. Small amounts of 50% solution of sodium hydroxide were dropped in at frequent intervals to keep the mixture alkaline. When all the dimethyl sulfate had been added the alkaline solution was boiled for one-half hour longer. The oily product was extracted with ether, washed and dried in the usual way. The oil remaining after evaporation of the ether distilled at 230–233° (757 mm.). A purer product was obtained by distillation under reduced pressure. The yields of *m*-methoxybenzaldehyde boiling at 129–130° (30 mm.) were about 70%. The condensation of this aldehyde and pyruvic acid was carried out exactly as described for the

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(3) Posner, *J. prakt. Chem.*, [2] **82**, 431 (1910).

(4) Hodgson and Beard, *J. Chem. Soc.*, **127**, 878 (1925).

corresponding condensation with benzaldehyde.[5] The potassium salt, separating in more than 90% yields from the reaction mixture, was washed with methyl alcohol and analyzed.

Anal. Calcd. for $C_{11}H_9O_4K$: K, 15.97. Found: K, 16.18.

From a cooled concentrated solution of the potassium salt, iced dilute hydrochloric acid precipitated a brilliant yellow acid in more than 80% yield. As the compound first precipitates as an oil, it is well to seed the solution with a few crystals of the acid prepared from a small sample of carefully purified potassium salt. The acid is readily soluble in the usual organic solvents. It separates from boiling water in fine yellow needles. A purer product is obtained by using boiling benzene, from which it separates in rosets of fine needles melting at 116–117°.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.85. Found: C, 64.22; H, 5.15.

Oxidation of this acid in sodium carbonate solution, with a slight excess of hydrogen peroxide, gave a 96% yield of *m*-methoxycinnamic acid. The yellow color of the original acid disappeared rapidly and the oxidation was complete in a few hours. From the potassium salt of *m*-methoxybenzalpyruvic acid, by the same procedure, yields of 87% of the cinnamic acid, calculated from the aldehyde used in the condensation, were obtained. This is a far better yield than could be obtained by either the Perkin or the Knoevenagel synthesis of this acid.

The methyl ester of *m*-methoxybenzalpyruvic acid was prepared by dissolving 5 g. of the finely ground pure acid in 30 cc. of methyl alcohol saturated with hydrogen chloride. After two to three minutes the methyl ester crystallized from the solution in long needles of a paler yellow than that of the acid. The same ester is obtained by action of diazomethane in an ethereal solution of the acid. It can be purified by crystallization from a small volume of methyl alcohol to which a few drops of water are added. It melts at 57°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.10; H, 5.78.

When 5 g. of acid was dissolved in 30 cc. of warm methyl alcohol saturated with hydrogen chloride and the mixture heated to boiling, no crystals separated from the solution on cooling. The reaction mixture was therefore poured into iced sodium carbonate solution. The heavy yellow oil which separated quickly solidified. The solid was dissolved in hot methyl alcohol and water added until the solution was faintly cloudy. The crystals that separated slowly were of two kinds, the yellow needles of the ester just described and large, clear, almost colorless, compact clumps. These were separated mechanically and repeatedly crystallized from a very small volume of methyl alcohol slightly diluted. The shining colorless crystals separate slowly in characteristic hexagonal prisms, melting at 72°. The compound is not affected by alkalies but is rapidly hydrolyzed to *m*-methoxybenzalpyruvic acid by boiling it in water to which a few drops of sulfuric acid have been added. It is the dimethyl acetal of the yellow ester just described, $CH_3OC_6H_4CH{=}CHC(OCH_3)_2COOCH_3$.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.76. Found: C, 63.18; H, 7.09.

Repeated attempts to prepare this substance from the ester were futile. It is evidently formed by the action of methyl alcohol and acid at a raised temperature with the ketone group of the acid, the product then esterifying. The yellow ester is formed at the same time. A partial separation of the two compounds may be made by repeated extraction of the mixture with small quantities of cold methyl alcohol, in which the yellow ester is sightly more soluble than the acetal.

The acetal group blocks the reaction of the ethylenic linkage so that the compound does not decolorize an acetone solution of potassium permanganate. This behavior led

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(5) Reimer, THIS JOURNAL, 53, 3147 (1931).

to the expectation that bromine might replace hydrogen of the ring instead of adding to the ethylenic linkage. The product of bromination was a bright yellow oil from which no pure substance could be obtained. Oxidation of this product with a hot solution of potassium permanganate gave a mixture of about equal quantities of *m*-methoxybenzoic and 6-bromo-3-methoxybenzoic acids, showing that the reaction had proceeded to a considerable extent in the direction looked for.

The ethyl ester of *m*-methoxybenzalpyruvic acid was prepared by dissolving the acid in ethyl alcohol saturated with hydrogen chloride. After standing for several hours, the clear solution was poured into iced sodium carbonate solution. The oil formed was extracted with ether, the ethereal solution washed, dried over sodium sulfate and the ether evaporated. The residue was a clear bright yellow oil.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.67; H, 6.00. Found: C, 66.39; H, 6.16.

No acetal was obtained in this reaction.

Reactions with Bromine

***m*-Methoxybenzalpyruvic Acid Dibromide,** *m*-$CH_3OC_6H_4CHBrCHBrCOCOOH$.—*m*-Methoxybenzalpyruvic acid was brominated in cooled chloroform solution. The decolorization was rapid and there was no evolution of hydrogen bromide until nearly the end of the reaction. The product separated from the chloroform in a thick paste if moist air was used, or in a semi-solid condition if the chloroform was evaporated in carefully dried air. The fact that this product is oily would seem to indicate a mixture of stereoisomers. The product lost hydrogen bromide so readily that all attempts at purification had to be abandoned.

β-Bromo-*m*-methoxybenzalpyruvic Acid, *m*-$CH_3OC_6H_4CH{=}CBrCOCOOH$, 166–167°.—This substance is prepared by shaking the oily product of the bromination reaction with cold water. A typical reaction was as follows: the colorless oily bromination product from 8.4 g. of pure *m*-methoxybenzalpyruvic acid was extracted, with vigorous shaking, with about 750-cc. portions of cold water. The liquid was filtered off and the residue further extracted until about 3 liters of water had been used. The clear filtrates gradually became cloudy and on standing overnight deposited a pure white crystalline compound. After another twenty-four hours further quantities of this substance separated from the filtrates. The reaction is evidently slow loss of hydrogen bromide from the dibromide in solution. From the solution were obtained in all about 90% yields of this substance, an unsaturated bromo acid. It is readily soluble in the usual organic solvents except ligroin. The purest samples are obtained from boiling benzene, from which it separates in stiff white needles melting at 166–167°.

Anal. Calcd. $C_{11}H_9O_4Br$: C, 46.31; H, 3.15. Found: C, 46.44; H, 3.43.

The acid dissolved in a small volume of 10% sodium carbonate solution from which, almost instantly, its shining sodium salt crystallized. When warmed or left standing in alkaline solution it slowly decomposed, a fragrant oil, probably a styrene derivative, being formed.

Oxidation of this acid in dilute sodium carbonate solution with potassium permanganate gave a nearly quantitative yield of *m*-methoxybenzoic acid, m. p. 105°, identified by a mixed melting point with this acid prepared by oxidation of *m*-methoxybenzaldehyde, thus proving the bromine to be in the side chain.

The methyl ester of β-bromo-*m*-methoxybenzalpyruvic acid was prepared by the action of an ethereal solution of diazomethane on the acid. It separates from methyl alcohol in fine, flattened needles melting at 95°.

Anal. Calcd. for $C_{12}H_{11}O_4Br$: C, 48.16; H, 3.68. Found: C, 47.83; H, 3.76.

Like the other β-bromobenzalpyruvic acids studied heretofore this ester could not be prepared by action of methyl alcohol saturated with hydrogen chloride.

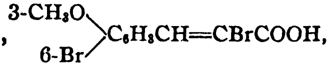
α-Bromo-*m*-methoxycinnamic Acid, *m*-$CH_3OC_6H_4CH{=}CBrCOOH$, 122°.—This compound is prepared by oxidation of the bromobenzalpyruvic acid just described. Five grams of this acid was suspended in 100 cc. of water and sufficient 10% sodium carbonate solution added to bring the acid into solution with vigorous shaking. Forty cc. of hydrogen peroxide (13 volumes) was now added, the mixture frequently shaken and allowed to stand at room temperature overnight. A second portion of 40 cc. of hydrogen peroxide was then added and the solution left for twenty-four hours. This long standing was necessary as the oxidation was found to proceed with unusual slowness. A slight cloudiness, probably due to the corresponding styrene derivative, was removed by repeated filtration, the solution cooled to 0° and dilute hydrochloric acid added, drop by drop, with vigorous stirring. The milky oil precipitating gradually solidified. The acid is readily soluble in methyl and ethyl alcohols, glacial acetic acid and chloroform, less readily in benzene. It can be purified by repeated crystallization from petroleum ether (b. p. 80–100°). By means of this solvent it can be separated from any admixture of the benzalpyruvic acid which may have escaped oxidation. It separates from boiling water in stiff fine needles of a faint cream color, melting at 122°. An 84% yield was obtained.

Anal. Calcd. for $C_{10}H_9O_3Br$: C, 46.70; H, 3.50. Found: C, 47.04; H, 3.82.

The acid is interesting in that it is not possible to obtain it from *m*-methoxycinnamic acid nor by condensation reaction.

The methyl ester was prepared by treatment of an ethereal solution of the acid with diazomethane. It is a clear pale yellow oil.

Anal. Calcd. $C_{11}H_{11}O_3Br$: C, 48.71; H, 4.06. Found: C, 48.53; H, 4.15.

α-Bromo-6-bromo-3-methoxycinnamic Acid,  $\begin{matrix}3\text{-}CH_3O\\6\text{-}Br\end{matrix}\!>\!C_6H_3CH{=}CBrCOOH$, 167–169°.—This acid is prepared by treating the cinnamic acid just described with one molecular proportion of bromine in cooled chloroform solution. The decolorization of the bromine proceeded slowly with copious evolution of hydrogen bromide. When all the bromine had been added, the solution was shaken vigorously until decolorization was complete. A crystalline product separated, which with more of the same substance crystallizing on evaporation of the solvent gave a 93% yield of product. The compound separates from boiling benzene in fine brittle needles very faintly cream-colored. It softens slightly at 163° and melts at 167–169°. It is readily soluble in cold methyl and ethyl alcohols and acetone and in hot chloroform and benzene. It is strongly triboelectric.

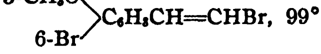
Anal. Calcd. $C_{10}H_8O_3Br_2$: C, 35.71; H, 2.38. Found: C, 35.77; H, 2.53.

On oxidation of this acid with potassium permanganate 6-bromo-3-methoxybenzoic acid was obtained.

The methyl ester separates in quantitative yield when the acid is warmed with methyl alcohol saturated with hydrogen chloride. It crystallizes from a small volume of hot methyl alcohol to which a few drops of water have been added in stiff, colorless needles melting at 79°.

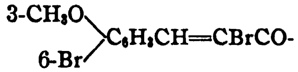
Anal. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.72; H, 2.86. Found: C, 37.80; H, 3.08.

Reaction with Excess of Bromine

α-Bromo-6-bromo-3-methoxystyrene,  $\begin{matrix}3\text{-}CH_3O\\6\text{-}Br\end{matrix}\!>\!C_6H_3CH{=}CHBr$, 99°.—*m*-Methoxybenzalpyruvic acid was treated with one molecular proportion of bromine as previously described and then a second molecular proportion of bromine added slowly. After twenty-four hours the solution was practically colorless. On evaporation of the solvent a yellowish, heavy oil was left. As no pure substance could be obtained from this it was dissolved in methyl alcohol, excess of potassium acetate added and the mixture boiled for one hour. The potassium bromide which had been separated was then filtered out, the alcohol distilled off, the product poured into water and the oily mixture extracted with ether. The clear yellow oil left on evaporation of the ether slowly deposited pale yellow crystals which were filtered out, washed with methyl alcohol and crystallized from a small volume of methyl alcohol. The substance separates in firm pale yellow stocky crystals melting at 99°. It is not soluble in sodium carbonate solution. It is readily soluble in benzene, acetone and ether, less readily in alcohol. Its acetone solution immediately decolorizes potassium permanganate solution. The properties are those of a styrene derivative.

Anal. Calcd. for $C_9H_8OBr_2$: C, 37.00; H, 2.75. Found: C, 37.24; H, 3.04.

From the yellow oil remaining no pure substance has been obtained.

β-Bromo-6-bromo-3-methoxybenzalpyruvic Acid,  $\begin{matrix}3\text{-CH}_3\text{O} \\ 6\text{-Br}\end{matrix}\!>\!\text{C}_6\text{H}_3\text{CH}{=}\text{CBrCO-}$ COOH.—Three grams of β-bromo-3-methoxybenzalpyruvic acid was added to 60 cc. of dry chloroform and 0.49 cc. of bromine added slowly. The bromine was decolorized with extreme slowness. After forty-eight hours of standing at room temperature and frequent shaking the solution was colorless. On evaporation of the solvent a colorless oil was left which gradually solidified. The oil was washed with small quantities of benzene. It was then dissolved in a small volume of cold chloroform to which an equal volume of low-boiling petroleum ether (30–60°) was added. The solution deposited colorless fine needles melting when pure at 137–139°. The substance is readily soluble in the usual organic solvents except low-boiling petroleum ether (30–60°). It may be crystallized from benzene. It readily decomposes on standing in solution.

Anal. Calcd. for $C_{11}H_8O_4Br_2$: C, 36.27; H, 2.20. Found: C, 36.33; H, 2.74.

On treatment in alkaline solution with excess of hydrogen peroxide the substance was very slowly oxidized to α-bromo-6-bromo-3-methoxycinnamic acid.

The methyl ester of this dibromomethoxybenzalpyruvic acid was prepared from an ethereal solution of the acid and diazomethane. It separates from ether in fine needles, from methyl alcohol in shining, stiff needles melting at 143°.

Anal. Calcd. for $C_{12}H_{10}O_4Br_2$: C, 38.10; H, 2.65. Found: C, 38.37; H, 2.31.

Reaction with Concentrated Sulfuric Acid.—When a sample of *m*-methoxybenzalpyruvic acid was stirred with a few drops of concentrated sulfuric acid, the yellow acid gave a dark reddish-brown solution changing rapidly to deep cherry-red. This color persists for many hours. The bromine derivatives of this acid gave none of the brilliant color reactions with sulfuric acid characteristic of the corresponding para- and ortho-methoxybromo compounds. The colors were pale yellow changing to brown with a faint pinkish tinge.

Summary

m-Methoxybenzalpyruvic acid and its reaction with bromine have been studied for the purpose of comparison with isomeric methoxybenzalpyruvic acids and with *m*-methoxycinnamic acid.

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[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES, ELI LILLY AND COMPANY]

A Study of the Effect of Unsaturated Aliphatic Groups in Barbituric Acids[1]

BY H. A. SHONLE AND JOHN H. WALDO

5,5-Dialkyl substituted barbituric acids containing such unsaturated groups as the allyl,[2] bromopropenyl,[3] crotyl,[4] propargyl,[5] isopropenylpropargyl,[5] cyclohexenyl[6] and cyclopentenyl[7] groups have been described and a number of them tested pharmacologically and used clinically.

Since barbituric acids containing the allyl group are, in general, more effective than those containing the propyl group, it was decided to establish experimentally whether barbituric acids containing larger unsaturated groups, such as the secondary pentenyl and secondary hexenyl groups, were more or less effective than barbituric acids containing the corresponding saturated groups. This study has been extended to include a comparison of barbituric acids containing the propargyl, propyl, allyl and bromopropenyl groups.

The saturated and unsaturated secondary alcohols employed in this investigation were prepared by the Grignard reaction. The propargyl alcohol was prepared by the method of Kirrmann.[8]

Since it has been pointed out previously that refluxing secondary alcohols with aqueous hydrobromic acid tends to cause a rearrangement which results in obtaining a mixture of isomeric bromides, we prepared the halides of all of the secondary alcohols used by saturating the cold alcohol with dry gaseous hydrobromic acid.[9] In order to prevent possible rearrangement during distillation, a low vacuum was used with the receiver immersed in liquid air so that distillation could be carried out without warming the flask above room temperature.[10] It was necessary to prepare 4-chloropentene-2 and 4-chlorohexene-2 instead of the bromide due to the instability of the latter. These chlorides were prepared by saturating the cold alcohol with dry hydrochloric gas.

That no rearrangement took place in the preparation of saturated halides by the above methods was experimentally established by the preparation of

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[1] Presented before the Division of Medicinal Chemistry at the New Orleans meeting of the American Chemical Society.

[2] T. B. Johnson and A. J. Hill, *Am. Chem. J.*, **46**, 537 (1911); E. Preisewerk and E. Grether, U. S. Patent 1,042,265 (1912); H. Hörlein and W. Kropp, U. S. Patent 1,056,793 (1913); E. H. Volwiler, THIS JOURNAL, **47**, 2236 (1925); A. W. Dox, U. S. Patent 1,615,870 (1927).

[3] F. Boedecker, U. S. Patent 1,622,129 (1927), and 1,739,622 (1929).

[4] L. Taub, L. Schütz and K. Meisenburg, U. S. Patent 1,511,919 (1924).

[5] M. Brockmühl and G. Ehrhart, U. S. Patent 1,682,062 (1928).

[6] W. Schulemann and K. Meisenburg, U. S. Patent 1,690,796 (1928).

[7] R. Chaux, *Compt. rend.*, **194**, 1193 (1932).

[8] A. Kirrmann, *Bull. soc. chim.*, [4] **39**, 698 (1926).

[9] M. L. Sherrill, B. Otto and L. W. Pickett, THIS JOURNAL, **51**, 3023 (1929); M. L. Sherrill, C. Baldwin and D. Haas, *ibid.*, **51**, 3034 (1929).

[10] Personal communication from Dr. M. S. Kharasch.

2- and 3-bromopentane, each of which had the refractive index as given by Sherrill.[9] From each of these bromides, barbituric acids were produced which differed from each other.

The mono- and di-substituted malonic esters were prepared and purified as previously described.[11] The barbituric acids were prepared by condensing the di-substituted malonic ester with urea in the presence of sodium ethylate. In one instance, propargyl bromide was condensed with *sec*-butylbarbituric acid to produce *sec*-butylpropargylbarbituric acid. The three tables give some of the constants of the products prepared.

TABLE I

HALIDES

Compound	B. p., °C.	n^{25}
4-Chloropentene-2	58 at 155 mm.	1.4311
4-Chlorohexene-2	73–76 at 136 mm.	1.4356
3-Bromohexane	65.8–67 at 49 mm.	1.4469 (n^{20})

TABLE II

DISUBSTITUTED MALONIC ESTERS[a]

Ethyl malonate derivatives	Boiling point °C. Mm.	Boiling point °C. Mm.	n^{25}
Isoamyl propargyl	142 at 11	to 151 at 14	1.4403 to 1.4409
1-Methylbutene-2 ethyl	135 at 15	to 138 at 15	1.4418 to 1.4438
1-Ethylbutene-2 ethyl	143.4 at 15	to 144.6 at 15	1.4437 to 1.4439
1-Ethylbutyl ethyl	135 at 9	to 132.8 at 8.5	1.4363 to 1.4369
sec-Butyl propyl	112 at 6	to 114 at 5	1.4331 to 1.4342

[a] The boiling points and refractive indices given are for the cuts which were found satisfactory for the desired synthesis.

TABLE III

DISUBSTITUTED BARBITURIC ACIDS

Derivative	Melting point °C. (Anschütz)	Nitrogen, % Calcd.	Nitrogen, % Found	
sec-Butyl propargyl	167 –168	12.61	12.52	12.44
Isoamyl propargyl	163 –164	11.86	12.00	12.20
1-Methylbutene-2 ethyl	114.5–116	12.50	12.51	12.58
1-Ethylbutene-2 ethyl	93 – 94	11.76	11.76	11.76
1-Ethylbutyl ethyl	112 –115	11.67	11.52	11.40
sec-Butyl propyl	136 –138	12.44	12.34	12.55

The several new barbituric acids described above and the known barbituric acids which were used for comparison were evaluated pharmacologically. Experience has indicated that it is unsatisfactory to compare data obtained at different times, or with different colonies of rats. Therefore we injected part of each group of rats with sodium isoamylethylbarbiturate. Freshly prepared two per cent. solutions of the sodium salt of the barbituric acids were injected intraperitoneally into white rats of 100 g. average weight and frequent observations were made until the animals either recovered or died. The pharmacologic data are summarized in

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(11) H. A. Shonle, A. K. Keltch and E. E. Swanson, THIS JOURNAL, 52, 2440 (1930).

Table IV, in which the minimum hypnotic dose, the minimum anesthetic dose, and the minimum lethal dose are given in milligrams per kilogram body weight.

TABLE IV

PHARMACOLOGICAL DATA

Barbituric acid	M. H. D. mg./kg.	M. A. D. mg./kg.	M. L. D. mg./kg.	Therap. index M. L. D./M. A. D.
1-Ethylbutyl ethyl	30	50	80	1.60
1-Ethylbutenyl-2 ethyl	50[a]	..	60[a]	..
1-Methylbutyl allyl	20	45	100	2.22
1-Methylbutyl ethyl	40	50	120	2.40
1-Methylbutenyl-2 ethyl	50[a]	90[a]	100	1.10
sec-Butyl allyl	40	60	110	1.84
Isoamyl propargyl	80	140	300	2.14
sec-Butyl propargyl	50	80	180	2.25
sec-Butyl bromopropenyl	70	..	120	..
sec-Butyl *n*-propyl	50	80	180	2.25

[a] Caused convulsions.

Discussion

The pharmacologic summary shows that when a saturated secondary pentyl or hexyl group in alkylethylbarbituric acid is replaced by an unsaturated group having the same carbon skeleton, a product having less satisfactory hypnotic properties is obtained. Both of the unsaturated secondary groups produced convulsions in white rats when low doses were given, and with higher doses either gave an unsatisfactory state of anesthesia or no anesthesia at all. The barbituric acids containing these unsaturated secondary groups were more toxic than the corresponding barbituric acids containing saturated groups and were also more toxic than the isomeric secondary alkyl allyl barbituric acids. The toxicity increased with the increasing molecular weight.

The isoamylpropargylbarbituric acid was less effective and less toxic than the *sec*-butylpropargyl. In this instance the derivative having the lower molecular weight was the more toxic. This increase of toxicity with the decrease in molecular weight is probably due to the presence of the more effective and the more toxic secondary butyl group. The *sec*-butylpropargyl and *sec*-butylpropylbarbituric acids were equally effective. It will be noted that the *sec*-butylallyl was the most effective of this series and the *sec*-butylbromopropenyl was the least satisfactory as shown by animal tests. There would appear therefore to be little correlation between the degree of unsaturation in the three carbon atom chain and the physiologic properties.

A more detailed report of other physiologic effects of these barbituric acids will be published in another journal.

We wish to thank Mr. E. E. Swanson and Mr. W. E. Fry for their care in carrying out the pharmacologic evaluation. We also wish to thank Mr.

Wilbur J. Doran for the micro-chemical nitrogen analyses reported in this investigation, and for his assistance in the preparation of some of the products.

Conclusion

1. Alkenylethylbarbituric acids containing the unsaturated secondary pentyl or hexyl group have less hypnotic action than corresponding barbituric acids with saturated alkyl groups and cause convulsions at low doses.

2. Two propargylalkylbarbituric acids were investigated and found to have hypnotic action which was not more effective than the corresponding barbituric acids containing the allyl or propyl group.

3. The following new products were prepared—isoamylpropargylmalonic ester, 1-methylbutenyl-2-ethylmalonic ester, 1-ethylbutenyl-2-ethylmalonic ester, 1-ethylbutylethylmalonic ester, *sec*-butyl-*n*-propylmalonic ester, *sec*-butylpropargylbarbituric acid, isoamylpropargylbarbituric acid, 1-methylbutenyl-2-ethylbarbituric acid, 1-ethylbutenyl-2-ethylbarbituric acid, 1-ethylbutylethylbarbituric acid and *sec*-butyl-*n*-propylbarbituric acid.

Indianapolis, Indiana

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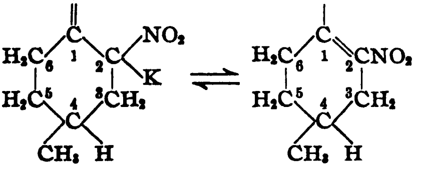
[Contribution from the Chemical Laboratory of the University of Illinois]

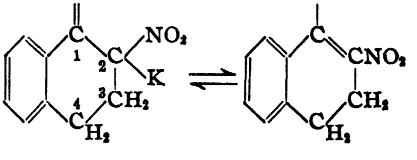
Asymmetric Syntheses. III. The Action of Optically Active Nitrates on α-Tetralone

By W. H. Horne and R. L. Shriner

The formation of an optically active product as the result of the reaction between 4-methylcyclohexanone and *d* or *l*-2-octyl nitrate[1] left undecided the location of the optically active center of the molecule and the exact structure of the salts of these nitro compounds. The presence of the asymmetric carbon atom at position 4 prevents any distinction between structures I and II since both forms would be optically active.



I II



III IV

In order to avoid the complicating effect of the asymmetric carbon atom at position 4, a study was made of the action of *d*- and *l*-2-octyl nitrates on another cyclic ketone, α-tetralone. If the potassium salt of the β-nitro-α-tetralone possesses the structure III, then any optical activity must be due to carbon number 2 and the salt is analogous to other optically active salts of secondary nitro compounds.[2] On the other hand, structure IV contains no asymmetric carbon atoms and would be optically inactive.

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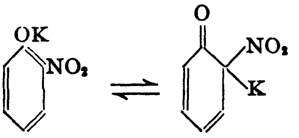
[1] Shriner and Parker, This Journal, 55, 766 (1933).

Treatment of α-tetralone with *d*- or *l*-2-octyl nitrates in the presence of potassium ethylate yielded potassium salts of β-nitro-α-tetralone which were optically inactive in every case. The reaction was carried out at 40, 22 and 0° but no activity could be observed. Immediate treatment of the potassium salt with acid gave the free β-nitro-α-tetralone, which was also optically inactive.

The optical inactivity of these compounds indicates that the structure of the salts of these nitro ketones is of the type shown by II and IV. Compounds of this type would be expected to resemble the salts of *o*-nitrophenol, most of whose reactions and properties indicate that they are derived from the enolic form (V) rather than the tautomeric keto form (VI)



V VI

Experimental

Phenylethyl Bromide.—By the action of 500 g. of 48% hydrobromic acid, 270 g. of concentrated sulfuric acid and 305 g. of phenylethyl alcohol there was obtained 375 g. (81.1%) of phenylethyl bromide, b. p. 77–80° at 3 mm.; 107–108° at 17 mm.

γ-Phenylbutyric Acid.—Twelve grams of sodium was dissolved in 250 cc. of absolute alcohol and 78 g. of malonic ester added. With vigorous stirring 89 g. of phenylethyl bromide was added and the resulting mixture refluxed for three hours. A solution of 130 g. of potassium hydroxide in 130 cc. of water was added and as much alcohol as possible removed by distillation. An additional 100 g. of 50% potassium hydroxide solution was added during the distillation of the alcohol. The residue was poured into 800 cc. of 20% hydrochloric acid and warmed on the steam cone. The layers were separated and the aqueous layer extracted with ether. The ether was distilled and the combined dry portions of the substituted malonic acid placed in a Claisen flask and heated in an oil-bath. Carbon dioxide evolution started at 120°. The temperature was slowly raised to 200° and maintained there for ten minutes. The γ-phenylbutyric acid was then vacuum distilled. The yield was 41 g. (52%) of colorless liquid boiling at 125–130° at 3 mm. This solidified and formed crystals melting at 52°, which checked the value reported in the literature.[3]

α-Tetralone.—A solution of 30 g. of γ-phenylbutyric acid in 200 cc. of concentrated sulfuric acid was heated in a boiling water-bath for three and one-half hours. The solution was poured on cracked ice and the resulting mixture extracted with ether.

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(2) Kuhn and Albrecht, *Ber.*, **60**, 1297 (1927); Shriner and Young, THIS JOURNAL, **52**, 3332 (1930).

(3) Rupe and Proske, *Ber.*, **43**, 1233 (1910).

The ether solution was dried and the ether distilled. Vacuum distillation of the residue yielded 13 g. (48.7%) of α-tetralone; b. p. 105° at 3 mm.; 135° at 26 mm. The oxime was prepared as a derivative and found to melt at 102–102.5°, which checked the value in the literature.[4]

***dl*-, *d*- and *l*-2-Octyl Nitrates.**—These were prepared according to the method previously described.[1] *dl*-2-Octyl nitrate boiled 96–98° at 20 mm.; n_D^{20} 1.4299. *d*-2-Octyl nitrate boiled 140–141° at 45 mm.; $[\alpha]_D^{25}$ +14.59; n_D^{20} 1.4301. *l*-2-Octyl nitrate boiled 100–103° at 24 mm.; $[\alpha]_D^{25}$ −14.64; n_D^{20} 1.4298.

Condensation of α-Tetralone with *dl*-2-Octyl Nitrate.—A solution of 4.5 g. of *dl*-2-octyl nitrate and 7.3 g. of α-tetralone in 70 cc. of absolute ether was added to a solution of potassium ethylate prepared from 1 g. of potassium, 8 g. of absolute ethyl alcohol and 25 cc. of absolute ether. The reaction mixture was maintained at 40° by means of a water-bath, after about twenty minutes 50 cc. of dry ether was added and the mixture allowed to stand for four hours. The precipitate was filtered and thoroughly washed with dry ether and alcohol mixture in order to remove a red condensation product. The yellow powder was dried after rapidly transferring to a vacuum desiccator containing concentrated sulfuric acid and a beaker of sodium hydroxide pellets. It could be purified by solution in methyl alcohol and reprecipitation with absolute ether.

Anal. Calcd. for $C_{10}H_8O_3NK$: K, 17.07; N, 6.11. Found: K, 16.32; N, 6.40.

Condensation of α-Tetralone with *d*-2-Octyl Nitrate and *l*-2-Octyl Nitrate.—Exactly the same procedure as above was followed using *d*-2-octyl nitrate and the optical rotation of the salt in absolute ethyl alcohol was determined immediately. It was optically inactive. The condensation was repeated using temperatures of 22 and 0° instead of 40° but no activity was observed.

Anal. Calcd. for $C_{10}H_8O_3NK$: K, 17.07; N, 6.11. Found: K, 17.34; N, 6.08.

d-Octanol-2 was recovered from the reaction mixture by fractional distillation of the filtrate obtained by removal of the salt. It boiled at 86–88° at 20 mm.; $[\alpha]_D^{25}$ +8.8°; n_D^{20} 1.4298.

Modification of this procedure by use of molecular quantities of α-tetralone and optically active nitrate and by addition of an ethereal solution of potassium ethylate to an ethereal solution of the nitrate and ketone also produced an optically inactive salt. The same result was obtained using *l*-2-octyl nitrate.

Anal. Calcd. for $C_{10}H_8O_3NK$: K, 17.07; N, 6.11. Found: K, 17.24; N, 6.15.

β-Nitro-α-tetralone.—The yellow precipitate obtained by the action of dilute hydrochloric acid upon an aqueous solution of the potassium nitro salt was found to melt at 67° after recrystallization from ethyl alcohol. It was optically inactive.

Anal. Calcd. for $C_{10}H_9O_3N$: N, 7.33. Found: N, 7.44.

Summary

Treatment of α-tetralone with *d*- and *l*-2-octyl nitrates in the presence of potassium ethylate produced optically inactive salts of β-nitro-α-tetralone.

URBANA, ILLINOIS

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[4] Kipping and Hill, *J. Chem. Soc.*, **75**, 144 (1899).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHEKIANG, CHINA]

Researches on Pyrimidines. The Molecular Rearrangement of Ethyl 2-Ethylmercapto-6-thiocyanopyrimidine-5-acetate[1,2]

BY YUOH-FONG CHI AND CHI MING MA

The starting point of this investigation on thiocyanates was ethyl 2-ethylmercapto-6-chloropyrimidine-5-acetate (I), which was prepared by interaction of phosphorus oxychloride with 2-ethylmercapto-6-oxypyrimidine-5-acetate.[3] The latter compound is easily obtained according to the method described by Johnson and Speh.[4] This chloropyrimidine reacts with potassium thiocyanate in benzene solution to form smoothly a normal rhodanide, II. Attempts to purify this latter pyrimidine derivative by distillation were unsuccessful as it was isomerized slowly into the isothiocyanate IV at its boiling point under 1 mm. pressure. That a normal thiocyanate structure is present is established by the behavior of the crude reaction product toward thioacetic acid. They interact to form ethyl 2-ethylmercapto-6-thiopyrimidine-5-acetate, III.

The isothiocyanate IV is easily prepared by refluxing the chloropyrimidine I with potassium thiocyanate in boiling toluene. This latter pyrimidine combines with alcohols, ammonia and aniline to form the corresponding thionurethans and thioureas, respectively. Prolonged exposure to the action of ammonia leads to the formation of 2-ethylmercapto-6-thioureapyrimidine-5-acetamide.

It has been the previous experience in our researches here that thiocyanates corresponding to formula II may be transformed into polymeric modifications by prolonged distillation. Such constructions apparently result from the polymerization of the isothiocyanate modification formed by isomerization. In the present case the isothiocyanate exhibits a behavior similar to that shown by Chi and Chen's 2-ethylmercapto-4-methyl-6-isothiocyanopyrimidine.[5] It is easily polymerized by prolonged heating at its boiling point, and the polymer is easily distinguished from the isothiocyanate form by its inactivity toward ammonia, amines and alcohol.

Experimental Part

$\overline{\mathrm{NC(SC_2H_5)=NCH=C(CH_2COOC_2H_5)CCl}}$, I, **Ethyl 2-Ethylmercapto-6-chloropyrimidine-5-acetate.**—Twenty-two grams of 2-ethylmercapto-6-oxypyrimidine-5-ace-

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(1) Our researches on pyrimidine thiocyanates were started originally in the Sterling Chemistry Laboratory of Yale University under the direction of Professor Treat B. Johnson.

(2) The work discussed in this paper has been accomplished and arranged for publication through the support of a grant from the Rockefeller Foundation of New York. The authors desire to express here their appreciation and heartiest thanks for this liberal assistance.

(3) Johnson, Peck and Ambler, THIS JOURNAL, 33, 758 (1911).

(4) Johnson and Speh, *Am. Chem. J.*, 38, 607 (1907).

(5) Chi and Chen, THIS JOURNAL, 54, 2056 (1932).

tate and 75 cc. of phosphorus oxychloride interacted at 100° to give a sirupy product which distilled, after washing with water and drying, at 174° at 4 mm. pressure and 168° at 2 mm. The yield was 17 g. or 70.3% of theoretical.

Anal. Calcd. for $C_{10}H_{13}O_2N_2SCl$: N, 10.75. Found: N, 10.63, 10.68.

$NC(SC_2H_5)=NCH=C(CH_2COOC_2H_5)=CSCN$, II, **ethyl 2-ethylmercapto-6-thiocyanpyrimidine-5-acetate** is obtained by digestion of the preceding chloropyrimidine with potassium thiocyanate in benzene solution for about ten hours. It was never obtained in a pure state and a specimen of the oil distilled under 1 mm. pressure as follows: Fraction I, 175–180°; II, 181–186°; III, 187–195°; IV, 196–204°. Each fraction responded to the reaction of an isothiocyanate when treated with ammonia, yielding a thiourea compound. That a thiocyanate form was present in the crude reaction product was evidenced by its behavior toward thioacetic acid. With this reagent it reacted to form ethyl 2-ethylmercapto-6-thiopyrimidine-5-acetate, $NHC(SC_2H_5)=NCH=C(CH_2COOC_2H_5)CS$, III. This was purified by crystallization from 95% alcohol and separated in the form of needles melting at 130–131° to an oil.

Anal. Calcd. for $C_{10}H_{14}O_2N_2S_2$: N, 10.85. Found: N, 11.03, 10.61, 10.5.

This same pyrimidine is formed by interaction of sodium sulfhydrate with the chloropyrimidine I.

Molecular Rearrangement of Ethyl 2-Ethylmercapto-6-thiocyanopyrimidine-5-acetate

$NC(SC_2H_5)NCH=C(CH_2COOC_2H_5)CNCS$, IV, **Ethyl 2-Ethylmercapto-6-isothiocyanopyrimidine-5-acetate.**—This is formed by digesting the corresponding chloropyrimidine I with potassium thiocyanate in toluene for twenty hours. The pyrimidine was obtained as an oil which distilled at 190–200° at 4 mm.

Anal. Calcd. for $C_{11}H_{13}O_2N_3S_2$: N, 14.84. Found: N, 14.50.

A specimen of the isothiocyanate was redistilled several times under diminished pressure, and slowly converted into a polymerized modification. This distilled as a viscous oil boiling at 220° at 4 mm. pressure. On cooling, this product finally solidified and was purified further by crystallization from a mixture of benzene and ether. It separated, on cooling, in the form of prisms melting at 140–141°. The pyrimidine can be digested with alcohol for hours without change, and does not interact with ammonia or aniline.

Anal. Calcd. for $(C_{11}H_{13}O_2N_3S_2)_x$: N, 14.84; S, 22.64. Found: N, 14.78, 14.61; S, 22.51.

DERIVATIVES PREPARED BY INTERACTION OF THE CRUDE ISOTHIOCYANATE IV WITH AMINES AND ALCOHOL

Compound	Formula	Solvent	M. p., °C.	Nitrogen, % Calcd.	Found	
Ethyl 2-ethylmercapto-6-thioureapyrimidine-5-acetate	$C_{11}H_{16}O_2N_4S_2$	Bz	135–136	18.66	18.63	
2-Ethylmercapto-6-thioureapyrimidine-5-acetamide	$C_9H_{13}ON_5S_2$	Alc.	230	25.82	25.62	25.80
2-Ethylmercapto-6-thioureapyrimidine-5-acetic acid	$C_9H_{12}O_2N_4S_2$	Alc.	220–221	20.58	20.54	20.53
Ethyl 2-ethylmercapto-6-phenylthioureapyrimidine-5-acetate	$C_{17}H_{20}O_2N_4S_2$	Alc.	112.5–113	14.89	14.85	14.66
2-Ethylmercapto-6-thionethylurethanpyrimidine-5-acetic acid	$C_{11}H_{15}O_3N_3S_2$	Alc.	146–148	13.95	13.93	14.01

Summary

1. Ethyl 2-ethylmercapto-6-chloropyrimidine-5-acetate interacts with potassium thiocyanate to form first a normal thiocyanate. The latter easily undergoes a normal molecular rearrangement to give ethyl 2-ethylmercapto-6-isothiocyanopyrimidine-5-acetate.

2. Several derivatives of this isothiocyanate have been prepared by the action of amines and ethyl alcohol.

HANGCHOW, CHEKIANG, CHINA

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[CONTRIBUTION FROM THE PLAUT RESEARCH LABORATORY OF LEHN & FINK, INC.]

The Alkyl Derivatives of Halogen Phenols and their Bactericidal Action. II. Bromophenols

BY EMIL KLARMANN, LOUIS W. GATES, VLADIMIR A. SHTERNOV AND PHILIP H. COX, JR.

Introduction

Continuing the investigation of the bactericidal properties of the alkyl derivatives of halogen phenols[1] we prepared and studied a number of bromophenol homologs. A complete series of normal *o*-alkyl derivatives of *p*-bromophenol was synthesized comprising the compounds up to and including the 2-*n*-hexyl-4-bromophenol. We directed our attention primarily to the derivatives of *p*-bromophenol, since the exhaustive investigation of the two homologous series of *o*- and *p*-chlorophenol derivatives disclosed an antibacterial superiority of the *p*-chloro series over the *o*-chloro series in almost all instances. It was logical to assume that similar conditions would obtain in the group of bromophenol derivatives, and this opinion was borne out in certain individual test cases.

We were interested in determining the germicidal action of this series of compounds upon a number of representative resistant pathogenic microörganisms belonging to different bacteriological groups. On the basis of the previously observed group parallelism in the susceptibility of different microörganisms to the action of compounds of several homologous series of phenol derivatives,[2] the following test organisms were selected for the bacteriological evaluation of the bromophenol derivatives: the Gram-negative *Eberthella typhi*, the Gram-positive *Staphylococcus pyogenes aureus*, the acid-fast *Mycobacterium tuberculosis* (*hominis*) and the fungus *Monilia albicans*. The method of cultivating the microörganisms and of performing the tests will be described elsewhere.

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(1) Klarmann, Shternov and Gates, THIS JOURNAL, 55, 2576 (1933).

(2) Klarmann, "The Antibacterial Action of Certain Classes of Phenol Derivatives and Its Quasi-specific Character," paper presented before the section of Medicinal Chemistry of the American Chemical Society, Washington, March, 1933.

Bactericidal Action of Alkyl Bromophenol Derivatives.—Table I and Fig. 1 illustrate the relation between the chemical constitution of the compounds of this class and their germicidal action (expressed in terms of minimum germicidal concentrations effective in ten minutes at 37°, and of the "phenol coefficients" calculated therefrom). One observes at first an increase of germicidal power with the increasing weight of the substituting normal alkyl radical, a phenomenon common to different classes of homologous phenol and polyphenol derivatives. One encounters here, too, the "quasi-specific" effect of the higher homologs referred to in our preceding paper on chlorophenol derivatives. With respect to *Eberthella typhi*, the germicidal efficacy reaches its maximum with the *n*-butyl derivative, and declines thereafter with the *n*-amyl compound; it continues to rise with respect to the other three test organisms to considerable heights without the evidence of a maximum being reached in the case of the 2-*n*-hexyl-4-bromophenol, except perhaps with regard to *Monilia albicans*. If it is permitted to conclude by analogy with the conditions encountered among the alkyl chlorophenol derivatives, the rise of the curve for *Staphylococcus aureus* and *Mycobacterium tuberculosis* probably continues beyond the *n*-hexyl abscissa.

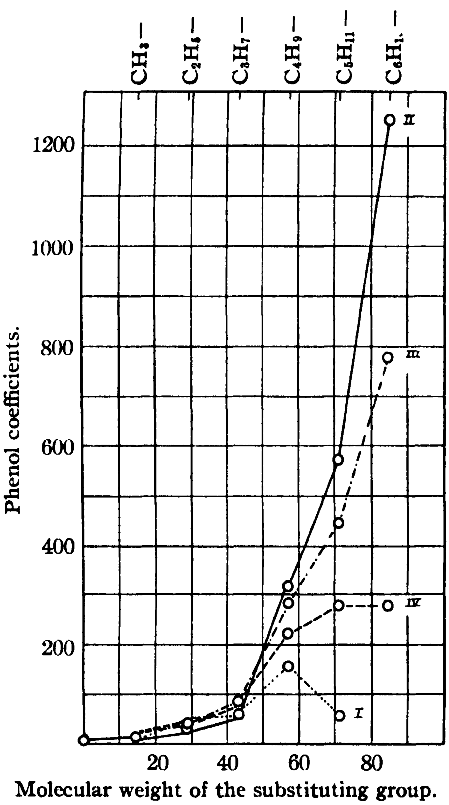

Fig. 1.—The germicidal action of *o*-alkyl derivatives of *p*-bromophenol. Test organisms: I.... *Eberthella typhi*; II—— *Staphylococcus pyog. aureus*; III·—·— *Mycobacterium tuberculosis* (*hom*); IV - - - *Monilia albicans*.

Considered *per se*, there are among the normal alkyl derivatives of *p*-bromophenol some highly effective agents whose bactericidal potency in the majority of cases compares favorably with or exceeds that of the corresponding chloro derivatives described in the preceding papers. Thus with respect to *Eberthella typhi*, the 2-*n*-butyl-4-bromophenol shows the greatest efficacy of the series. It surpasses that of 2-*n*-butyl-4-chlorophenol and approaches that of 2-*n*-amyl-4-chlorophenol. Against *Staphy-*

TABLE I

GERMICIDAL ACTION OF HOMOLOGOUS DERIVATIVES OF BROMOPHENOL

Minimum Concentrations Effective in 10 Min. (I) and Phenol Coefficients (II)

2-Alkyl derivatives of 4-bromophenol	*Eberthella typhi*		*Staphylococcus pyog. aureus*		*Mycobacterium tuberculosis (hom.)*		*Monilia albicans*	
	I	II	I	II	I	II	I	II
p-Bromophenol	1: 900	6.0	1: 400	5.0	1: 500	5.6	1: 500	6.3
Alkyl radicals								
Methyl	1: 2,000	12.5	1: 900	11.3	1: 1,200	13.3	1: 1,200	13.3
Ethyl	1: 5,000	31.3	1: 2,000	25.0	1: 2,500	27.8	1: 2,500	27.8
n-Propyl	1:10,000	62.5	1: 5,000	62.5	1: 7,000	77.8	1: 7,000	77.8
n-Butyl	1:25,000	156	1: 25,000	313	1:25,000	278	1:20,000	222
n-Amyl	1:10,000	625	1: 40,000	571	1:40,000	444	1:25,000	278
sec-Amyl	<1: 5,000	> 33	1: 12,000	150	1:14,000	156	1:12,000	150
n-Hexyl	....	...	1:100,000	1250	1:70,000	778	1:25,000	278
Cyclohexyl	<1: 3,500	> 23	1: 30,000	429	1:25,000	278	1:20,000	222
Alkyl derivatives of 2-bromophenol								
o-Bromophenol	1: 500	3.3	1: 250	3.1	1: 350	3.9	1: 300	3.8
Alkyl radicals								
4-*tert*-Amyl-	1: 5,000	33.3	1: 12,000	150	1:10,000	100	1: 7,000	77.8
4-*n*-Hexyl-	<1: 3,000	> 20	1: 50,000	625	1:50,000	556	1:20,000	222
4-*n*-Propyl-3,5-dimethyl-	indef.	indef.	1: 25,000	357	1:20,000	222	1:11,000	138
Phenol (control)	1:140-160	1	1: 70-80	1	1:90-100	1	1: 80-90	1

lococcus aureus, the *n*-butyl and *n*-amyl derivatives of *p*-bromophenol are more effective than those of *p*-chlorophenol, while the *p*-chloro and *p*-bromo derivatives of *o*-*n*-hexylphenol show practically the same efficacy. With respect to *Mycobacterium tuberculosis*, the entire series of *n*-alkyl-*p*-bromophenol derivatives surpasses the corresponding *p*-chlorophenol series.[2] As to *Monilia albicans*, the same is true of the members of the series up to and including the *n*-butyl derivative, while the opposite is true of the higher normal homologs studied.[2]

The effect of *o*-cyclohexyl-*p*-bromophenol upon *Staphylococcus aureus* and *Mycobacterium tuberculosis* is comparable to that of the corresponding chlorophenol derivative; it is lower with regard to *Monilia albicans*.

The comparison of the unsubstituted *p*-bromophenol with *o*-bromophenol discloses a bactericidal superiority of the former.[3] As might have been expected from the comparison of the bacteriological effects of the compounds of the *o*-alkyl-*p*-chloro series with those of the *p*-alkyl-*o*-chloro series,[1] which indicates a greater germicidal potency of the former, the 2-*n*-hexyl-4-bromophenol is a more potent germicide than the 4-*n*-hexyl-2-bromophenol.

4-*tert*-Amyl-2-bromophenol appears to be generally more effective than the corresponding chlorophenol derivative.

Finally, if it is remembered that the phenolic hydroxyl group is most likely to be concerned primarily in bringing about the germicidal effect, and that therefore one would be justified in placing the quantitative

(3) Klarmann, Shternov and Von Wowern, *J. Bacteriol.*, **17**, 427 (1929).

consideration of the relationship between chemical constitution and germicidal action upon a basis of molecular equivalents rather than upon one of simple weight relations, the conclusion is justified (disregarding some exceptions) that the introduction of one bromine atom into the nucleus of phenol and its homologs leads to more potent germicides than the entrance of a chlorine atom.

Note.—The comments expressed in our preceding paper as to a potential usefulness of some of the compounds described therein, in the chemotherapy of certain infections, seem to apply to the several substituted bromophenols as well.

The pharmacological investigation of the homologous bromophenol series is in progress at this time.

By way of advance published information, enough experimental material has been obtained by us to show that the "quasi-specific" germicidal effect of substituted chloro and bromophenols of higher molecular weight is not an isolated characteristic of the two series of compounds under consideration, but, rather that, it appears to be a general phenomenon, common to certain members of different classes of phenol and polyphenol derivatives.

Notes on the Preparation of the Substituted Bromophenols.—The methods employed in the preparation of the bromophenol derivatives correspond closely to those described in the preceding paper for the chloro compounds; *i. e.*, all *o*-*n*-alkyl derivatives (with the exception of the methyl compound) were prepared by the reduction of the corresponding bromohydroxyphenyl alkyl ketones, the latter having been obtained by intramolecular rearrangement of the corresponding bromophenyl esters.

The secondary amyl derivative was made by direct condensation of *p*-bromophenol with *n*-amyl alcohol in the presence of zinc chloride.

The *o*-methyl and *o*-cyclohexyl derivatives of *p*-bromophenol were prepared by direct bromination.

The same method was applied in introducing bromine in the *o*-position of the following alkyl phenol derivatives: 4-*tert*-amyl-, 4-*n*-propyl-3,5-dimethyl- and 4-*n*-hexylphenol.

Preparation of *o*-*n*-Alkyl Derivatives of *p*-Bromophenol. Example: Preparation of 2-*n*-Hexyl-4-bromophenol.—Caproyl chloride (47.8 g.) was added to 58 g. of *p*-bromophenol and the mixture allowed to stand overnight. It was treated with warm water, dried and distilled *in vacuo*. The pure *p*-bromophenyl caproate distilled at 139–140° at 2 mm.

This ester was rearranged to the corresponding 5-bromo-2-hydroxycaprophenone by means of anhydrous aluminum chloride; 75 g. of the ester and 36.3 g. of the aluminum chloride were heated in an oil-bath at 150–160° for thirty minutes. The mixture thus obtained was treated with cold water and dilute hydrochloric acid. The suspended precipitate was taken up in ether and the ether solution washed repeatedly with water. After evaporation of the solvent, the residue was recrystallized from isopropyl alcohol.

This 5-bromo-2-hydroxycaprophenone was reduced to the corresponding 2-*n*-hexyl-4-bromophenol by means of amalgamated zinc and 15% hydrochloric acid. The product was purified by vacuum distillation. It solidified on standing and was recrystallized from heptane.

Preparation of Alkyl Derivatives of *o*-Bromophenol. Example: Preparation of 4-*tert*-Amyl-2-bromophenol.—*p*-*tert*-Amylphenol (41 g.) was dissolved in 100 cc. of carbon tetrachloride. To this a solution of 40.8 g. of bromine in 25 cc. of carbon tetrachloride was added drop by drop. The reaction mixture was allowed to stand overnight and was warmed gently the next morning. The solvent was removed by steam distillation, the residue was diluted with ether, washed with water and a solution of sodium bicarbonate, dried with sodium sulfate and, after removal of the ether, distilled in a vacuum.

Preparation of *o*-Isoalkyl Derivatives of *p*-Bromophenol. Example: Preparation of 2-*sec*-Amyl-4-bromophenol.—*p*-Bromophenol (86.5 g.), 83 g. of zinc chloride, 15 g. of concentrated hydrochloric acid and 31 g. of *n*-amyl alcohol were heated to mild boiling under reflux for two hours, whereupon a mixture of 62 g. of *n*-amyl alcohol and 5 g. of concentrated hydrochloric acid was allowed to flow in drop by drop. After gentle refluxing for another six hours the mixture was poured into ice-cold water. After addition

TABLE II

PHYSICAL AND ANALYTICAL DATA OF THE SUBSTITUTED BROMOPHENOLS AND THEIR INTERMEDIATES

2-Alkyl derivatives of 4-bromophenol	Formula	B. p., °C.	Mm.	M. p., °C.	Bromine, % Calcd.	Bromine, % Found
Methyl-[a]	$CH_3(2)Br(4)C_6H_3OH$	118–123	7	63.5		
Ethyl-	$C_2H_5(2)Br(4)C_6H_3OH$	110	3		39.76	40.17
n-Propyl-	n-$C_3H_7(2)Br(4)C_6H_3OH$	113–117	3	42.0	37.17	37.14
n-Butyl-	n-$C_4H_9(2)Br(4)C_6H_3OH$	125–127	2	43.5	34.89	34.41
n-Amyl-	n-$C_5H_{11}(2)Br(4)C_6H_3OH$	143–145	3	36	32.88	33.16
sec-Amyl-	*sec*-$C_5H_{11}(2)Br(4)C_6H_3OH$	134–138	4		32.88	32.69
n-Hexyl-	n-$C_6H_{13}(2)Br(4)C_6H_3OH$	150–152	4	53.6	31.09	31.36
Cyclohexyl-	cyclo-$C_6H_{11}(2)Br(4)C_6H_3OH$	167	5	43.8	31.34	31.39
Alkyl derivatives of 2-bromophenol						
4-*tert*-Amyl-	*tert*-$C_5H_{11}(4)Br(2)C_6H_3OH$	122	4		32.88	32.76
4-*n*-Propyl-3,5-dimethyl-	n-$C_3H_7(4)(CH_3)_2(3,5)Br(2)C_6HOH$			91.3	32.88	32.39
4-*n*-Hexyl-	n-$C_6H_{13}(4)Br(2)C_6H_3OH$	148	7		31.09	31.59
Ketones (intermediates) 5-bromo-2-hydroxy-						
Acetophenone[b]	$CH_3{\cdot}CO{\cdot}C_6H_3Br(5)OH(2)$			57.3	37.17	37.26
Propiophenone	$C_2H_5{\cdot}CO{\cdot}C_6H_3Br(5)OH(2)$			76.0	34.90	34.70
Butyrophenone	n-$C_3H_7{\cdot}CO{\cdot}C_6H_3Br(5)OH(2)$	127–132	3	53.6	32.89	32.61
Valerophenone	n-$C_4H_9{\cdot}CO{\cdot}C_6H_3Br(5)OH(2)$	127–136	2		31.10	31.56
Caprophenone	n-$C_5H_{11}{\cdot}CO{\cdot}C_6H_3Br(5)OH(2)$			60.5	29.49	29.38
Esters (intermediates), 4-bromophenyl-						
Acetate[c]	$CH_3CO_2{\cdot}C_6H_4Br(4)$	100	2		37.17	37.32
Propionate	$C_2H_5CO_2{\cdot}C_6H_4Br(4)$	113	3		34.90	35.41
Butyrate	n-$C_3H_7CO_2{\cdot}C_6H_4Br(4)$	112	2		32.89	33.98
Valerate	n-$C_4H_9CO_2{\cdot}C_6H_4Br(4)$	134–138	4		31.10	31.54
Caproate	n-$C_5H_{11}CO_2{\cdot}C_6H_4Br(4)$	139–140	2		29.49	29.93

[a] Previously prepared by Claus and Jackson, *J. prakt. Chem.*, [2] 38, 324 (1888); Zincke and Hedenstroem, *Ann.*, 350, 273 (1906); Goldschmidt, Schulz and Bernhard, *ibid.*, 478, 1 (1930); Raiford and Couture, THIS JOURNAL, 44, 1793 (1922).

[b] Previously prepared by Claus, German Patent 96,659 (1897); v. Kostanecki and Ludwig, *Ber.*, 31, 2953 (1898); Feuerstein and Kostanecki, *ibid.*, 31, 716 (1898).

[c] Previously prepared by Wohlleben, *ibid.*, 42, 4374 (1909); Autenrieth and Muehlinghaus, *ibid.*, 40, 746 (1907).

of ether the aqueous portion was discarded and the ethereal layer treated as in the preceding example.

Hydrochloric acid in zinc chloride condensation has been used by R. R. Read.[4]

In the bacteriological part of this work we were assisted by Mr. A. Grawehr of our laboratory staff, whose efficient collaboration is herewith gratefully acknowledged.

Summary

The investigation of the antibacterial properties of homologous halogen phenol derivatives is being continued. A number of alkylbromophenol derivatives were prepared and tested bacteriologically. Among them are a complete series of *o*-*n*-alkyl compounds of *p*-bromophenol up to the *n*-hexyl compound, the *o*-*sec*-amyl and the *o*-cyclohexyl derivatives of *p*-bromophenol and several para substituted *o*-bromophenol compounds, such as the *p*-*tert*-amyl-, *p*-*n*-hexyl- and *p*-*n*-propyl-*m*-dimethyl-derivatives of *o*-bromophenol.

Four pathogenic microörganisms were used in the bacteriological experiments, *viz.*, *Eberthella typhi*, *Staphylococcus pyogenes aureus*, *Mycobacterium tuberculosis* (*hom.*) and *Monilia albicans*. This selection of four representative test organisms was based on the observation of a "group-parallelism" in the susceptibility of a larger number of microörganisms to the action of the substituted halogen phenol derivatives; it implies a qualitative and quantitative similarity in the germicidal effect of the compounds in question upon the members of various groups of microörganisms such as the typhoid-colon group, the group of pathogenic cocci, the group of acid fast bacteria and the group of pathogenic fungi.

When tested with the aid of these microörganisms the substituted bromophenol derivatives were found to be strongly germicidal and to compare favorably in this respect with the chloro derivatives studied previously. As in the latter case the constitution of the molecule and the weight of the substituents not only influence the intensity of the germicidal action, but also determine the point at which the "quasi-specific" effect becomes apparent, *i. e.*, where the germicidal action of a given compound with respect to the Gram-negative *Eberthella typhi* (and also other organisms of the colon-typhoid group) declines or practically disappears while at the same time reaching very considerable heights with regard to pathogenic cocci (as represented by *Staphylococcus aureus*), acid-fast bacteria (represented by *Mycobacterium tuberculosis*) and pathogenic fungi (represented by *Monilia albicans*).

BLOOMFIELD, NEW JERSEY

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(4) Read, U. S. Patent 1,887,662, Nov. 15, 1932.

[CONTRIBUTION FROM THE DIVISION OF HORTICULTURAL CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

Isolation and Identification of the Organic Nitrogenous and Non-Nitrogenous Compounds Occurring in the Alaska Pea. I. The Presence of Citric Acid in the Alaska Pea

BY S. L. JODIDI

From the work of Osborne and his associates[1] we know the proteins, and from that of Jodidi,[2] Boswell,[3] and Schulze,[4] we know the classes of compounds other than proteins which occur in the pea (*Pisum sativum*). The presence of citric acid in peas was reported by Ritthausen,[5] who has isolated the acid by a method *different* from the one used by the writer, namely, by extracting peas with acidified water, neutralizing the extract and precipitating the acid with lead acetate. He did not mention the *variety* of peas used by him. Yet different varieties differ in their chemical composition. Nor did he give the *quantity* of citric acid present in peas, all of which are given in this paper.

Experimental Part

The peas employed were of the Alaska variety used chiefly by the canning industry. The seed, which was of size 2, was dried rapidly in a specially constructed forced-draft drying apparatus at the temperature of 60–65° to prevent enzymic action and ground to pass a 40-mesh sieve. The average percentage composition of the pea meal was as follows: dry matter, 92.90; ash, 3.88; fat (ether extract), 1.79; total nitrogen (Kjeldahl), 4.48; protein nitrogen (Stutzer method), 2.16; reducing sugars, 0.19; sucrose, 15.92; starch, 31.51—all calculated on the basis of the water-free meal.

One hundred gram portions of the meal were treated with 900 to 1000 cc. of distilled water at 55°, toluene being added to prevent bacterial action. The flasks with their contents were allowed to stand at that temperature for about four hours, being shaken occasionally. The mash was then filtered off with suction. The cake remaining on the filter was pressed out well and the juice thus obtained was added to the main extract. The slightly turbid filtrates were refiltered until clear, when they were evaporated to dryness *in vacuo*. Altogether 750 g. of the pea meal was worked up as described.

The dry residue obtained from the aqueous extract of the peas was now repeatedly boiled out with absolute alcohol under reflux, allowed to cool for some time and filtered. On standing the filtrates ordinarily became cloudy or gave precipitates which were filtered out and combined with the bulk of the substance found to be insoluble in absolute alcohol. The combined clear wine-red filtrates were then evaporated to dryness under reduced pressure, the dry residues again boiled out with absolute alcohol, filtered and the clear filtrates evaporated in a vacuum. The extraction with absolute alcohol and evaporation was repeated once more. The final residue obtained was easily soluble in water, fairly soluble in alcohol, and very difficultly soluble in ether. This residue was

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(1) Osborne and co-workers, THIS JOURNAL, **18**, 583 (1896); **20**, 348, 410 (1898); *J. Biol. Chem.*, **3**, 213 (1907).

(2) Jodidi, *J. Agr. Research*, **43**, 811 (1931).

(3) Boswell, *Maryland Agr. Expt. Sta. Bull.*, 306 (1929).

(4) Schulze, *Landw. Vers.-Stat.*, **39**, 269 (1891); **46**, 23 (1895); *Z. physiol. Chem.*, **15**, 140 (1890–91).

(5) Ritthausen, *J. prakt. Chem.*, **29**, 357 (1884).

assumed to contain proline, which is the only amino acid that is soluble in absolute alcohol. With this in mind we prepared the copper salt by dissolving the bulk of the residue in water, boiling the solution with an excess of freshly prepared copper hydroxide for half an hour and evaporating the filtrate from the excess copper hydroxide to dryness in a vacuum. The copper salt was found to be readily soluble in water, fairly soluble in hot alcohol and apparently insoluble in ether. However, to our surprise the solution of the copper salt in water showed a pretty *green* color, while the copper salt of proline in aqueous solution is known to have a deep *blue* color. On further examination it was found that the aqueous solution of the residue showed a strongly acid reaction, while the solution of proline in water has a very slight acid reaction. It was now evident that the substance in hand is not proline. In order to establish the identity of the substance, the copper salt was dissolved in water, decomposed with hydrogen sulfide, and the filtrate from copper sufilde evaporated to dryness under diminished pressure. Twice recrystallized and dried for several hours in the oven the substance melted at 153°. Water-free citric acid melts at 153–154°. At this point it seemed of interest, from the standpoint of identification, to prepare the copper salt of citric acid. Several grams of Kahlbaum citric acid was dissolved in water and boiled with freshly precipitated copper hydroxide, the excess being filtered out. The filtrate showed a *green* color and the other properties observed on the copper salt of the isolated substance.

The Calcium Salt.—It was prepared by dissolving the isolated substance in water to which calcium chloride and ammonia was added and the whole boiled. The precipitate obtained was filtered off while boiling hot and washed with boiling hot water. The precipitate was then dried in the air for several days until its weight became constant. For the moisture estimation the air-dry substance was dried at 190°.

Anal. Calcd. for $[C_6H_5O_7]_2Ca_3 + 4H_2O$: H_2O, 12.63. Found: H_2O, 12.70 and 12.81.

For the calcium estimation the air-dry substance was first heated over the Bunsen burner and finally over the blast burner.

Anal. Calcd.: CaO, 29.45. Found: 29.39 and 29.56.

Summary

By repeatedly extracting the evaporated aqueous extract of Alaska pea with absolute alcohol and by treating the alcoholic extracts in a definite way as outlined in this paper, citric acid was obtained. It was identified by its acid reaction, the melting point, the properties of the copper salt, and by the analysis of its calcium salt. The quantity of citric acid found was equal to 0.36% of the oven-dried peas.

WASHINGTON, D. C.

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[CONTRIBUTION NO. 125 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XVII. Mercury Derivatives of Vinylacetylene

BY WALLACE H. CAROTHERS, RALPH A. JACOBSON AND GERARD J. BERCHET

As a means of identifying true acetylenic compounds the derivatives formed by the action of K_2HgI_4 are useful since they are generally crystalline and have definite melting points.[1] When this reagent is applied to vinylacetylene (I) it furnishes di-vinylethynyl-mercury (II), which separates from alcohol in the form of white leaflets melting at 144 to 145°. The compound is readily soluble in chloroform, but on standing in the air for twenty-four to forty-eight hours it becomes yellow in color and insoluble in chloroform. Analysis indicates that considerable amounts of oxygen are absorbed during this transformation. The oxidized product does not melt, but sometimes explodes on being heated or subjected to mechanical shock.

Di-vinylethynyl-mercury undergoes the following transformations. Cold dilute hydrochloric acid regenerates the vinylacetylene; chlorine and bromine yield the α-chloro- and bromo-vinylacetylenes (III); and metallic sodium in dry benzene produces sodium vinylacetylide.

Di-vinylethynyl-mercury is also produced by the action of mercuric acetate in acetic acid on vinylacetylene at ordinary temperatures, but if the temperature is raised to 60 or 70° reaction proceeds further with the formation of a compound whose composition and chemical behavior agree with that required for 1,1-di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene (IV). The same product is obtained by treating di-vinylethynyl-mercury with mercuric acetate in acetic acid at 60 to 70°.[2]

$CH_2{=}CH{-}C{\equiv}CH$ (I)

$(CH_2{=}CH{-}C{\equiv}C)_2Hg$ (II)

$CH_2{=}CH{-}C{\equiv}CX$ (III)

$CH_2{=}CH{-}(CH_3COOHgO)C{=}C(HgOOCCH_3)_2$ (IV)

$CH_2{=}CH{-}CO{-}CH_3$ (V)

$CH_2{=}CH{-}CO{-}CBr_3$ (VI)

$CH_2{=}CH{-}(OHgX)C{=}C(HgX)_2$ (VII)

This compound is a white crystalline solid somewhat soluble in water and more soluble in dilute acetic acid. It is infusible. By the action of hydrochloric acid it is decomposed with the formation of methyl vinyl ketone (V). Similarly by the action of bromine it is converted into tribromomethyl vinyl ketone (VI). The action of potassium iodide, bromide or chloride on IV causes replacement of the acetyl groups by halogen

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(1) Johnson and McEwen, THIS JOURNAL, 48, 469 (1926).

(2) Myddleton, Barrett and Seager, *ibid.*, 52, 4405 (1930), have presented evidence favoring the general structure $-C(OHgOAc){=}C(HgOAc)_2$ for the products obtained by the action of mercuric acetate on monosubstituted acetylenes.

and gives insoluble products corresponding in composition with the general formula VII.

Di-vinylethynyl-mercury.—The addition of an alcoholic solution of vinylacetylene to an excess of the alkaline mercuric iodide reagent[1] yielded a copious precipitate. This was filtered off and crystallized from boiling absolute alcohol. It separated in the form of white leaflets melting at 144 to 145°.

Anal. Calcd. for C_8H_6Hg: Hg, 66.25. Found: Hg, 66.46, 66.35.

The same compound was obtained by adding vinylacetylene (30 g.) to a cold solution of 5 g. of mercuric oxide in 250 cc. of acetic acid.

Anal. Calcd. for C_8H_6Hg: C, 31.72; H, 1.99. Found: C, 32.00; H, 2.46.

Upon standing for forty-eight hours the di-vinylethynyl-mercury became yellow in color and insoluble in chloroform. It had also acquired the ability to explode under the action of heat or mechanical shock. Analysis of this explosive product showed the presence of only 27.70% carbon and 2.23% hydrogen.

Freshly prepared di-vinylethynyl-mercury reacted with bromine or iodine to give the corresponding bromo- and iodo-vinylacetylenes. In one experiment 23.5 g. of the mercury compound in 177 cc. of chloroform was treated slowly with a 10% solution of bromine in chloroform; 22.64 g. of bromine was absorbed before decolorization ceased. The chloroform was removed, and distillation of the residue (11 g.) then gave 3 g. of 1-bromo-2-vinylacetylene, b. p. 50 to 52° at 210 mm. (see p. 4667).

1,1-Di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene (IV).—A solution of 5.2 g. of vinylacetylene in 100 cc. of acetic acid was added to a solution of 86.6 g. of mercuric oxide in 700 cc. of acetic acid surrounded by a water-bath at 45°. After one-half hour the temperature of the bath was increased to 60° and maintained between 60–70° for four hours. During this period a white crystalline solid separated. The mixture was filtered and the solid (79 g.) crystallized from dilute acetic acid; yield 93.4%. The product was somewhat soluble in water, more so in dilute acetic acid, but insoluble in the common organic solvents.

Anal. Calcd. for $C_{10}H_{12}O_7Hg_3$: C, 14.18; H, 1.43; Hg, 71.15. Found: C, 14.14; H, 1.95; Hg, 70.72.

1,1-Di-iodomercuri-2-iodomercurioxy-1,3-butadiene.—To a hot solution of 4 g. of 1,1-diacetoxymercuri-2-acetoxymercurioxy-1,3-butadiene in 100 cc. of 50% acetic acid was added slowly with stirring 2.8 g. of potassium iodide in 20 cc. of water. The yellow precipitate was filtered, washed several times with hot 50% acetic acid, then with water, and finally with acetone. The pale yellow solid was insoluble in water and in the common organic solvents.

Anal. Calcd. for $C_4H_3OHg_3I_3$: Hg, 57.34; I, 36.28. Found: Hg, 55.22, 55.47; I, 36.27, 36.45.

1,1-Di-bromomercuri-2-bromomercurioxy-1,3-butadiene was obtained in a similar manner from potassium bromide as a white solid insoluble in water and in the common organic solvents.

Anal. Calcd. for $C_4H_3OHg_3Br_3$: Hg, 66.23; Br, 26.37. Found: Hg, 67.82, 68.14; Br, 25.18, 25.29.

1,1-Di-chloromercuri-2-chloromercurioxy-1,3-butadiene was obtained in a similar manner from potassium chloride as a white solid insoluble in water and in the common organic solvents.

Anal. Calcd. for $C_4H_3OHg_3Cl_3$: Cl, 13.72. Found: Cl, 14.38.

Hydrolysis of 1,1-Di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene.—To 423 g. of the mercury compound (0.5 mole) in 200 cc. of water was added 300 cc. of hydrochloric acid (37%). After three hours, a small amount of hydroquinone was added, and the solution distilled until the distillate amounted to 300 cc. From the latter, pure methyl vinyl ketone was isolated by ether extraction and distillation. With phenylhydrazine it gave the known derivative phenyl-1-methyl-3-pyrazoline melting at 76°.[3]

Action of Bromine on 1,1-Di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene.—Bromine (239 g.) was slowly added to a suspension of 285 g. (0.337 mole) of the mercury compound in 700 cc. chloroform until decolorization was complete. Cooling was required to maintain the temperature below 60°. After standing, the mixture was filtered, washed with 10% hydrochloric acid and with water and distilled. At 0.5 mm. 44 g. of a yellow viscous liquid boiling at 128–130° was obtained. On standing for forty-eight hours it solidified. Three crystallizations from petroleum ether gave white rectangular plates melting at 73–75°. Although additional crystallizations did not alter the melting point, the product was not analytically pure. However, the ease with which bromoform was liberated when the crystals were warmed with dilute alkali indicates that the product was mainly tribromomethyl vinyl ketone contaminated perhaps with dibromomethyl vinyl ketone.

Anal. Calcd. for $C_4H_3OBr_3$: C, 15.64; H, 0.98; Br, 78.15. Found: C, 16.42, 16.85; H, 1.89, 1.75; Br, 72.18, 71.89.

Summary

Vinylacetylene when treated with potassium mercuri-iodide or with mercuric acetate at the ordinary temperature yields di-vinylethynyl-mercury, a crystalline solid melting at 144 to 145°. The action of mercuric acetate on vinylacetylene at 60 to 70° yields 1,1-di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene. Some reactions of these compounds are described.

WILMINGTON, DELAWARE

RECEIVED JULY 21, 1933
PUBLISHED NOVEMBER 7, 1933

(3) Maire, *Bull. soc. chim.*, (4) 3, 272 (1908).

[CONTRIBUTION NO. 126 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & CO.]

Acetylene Polymers and their Derivatives. XVIII. 1-Halogen-2-vinylacetylenes

BY RALPH A. JACOBSON AND WALLACE H. CAROTHERS

By the action of alkaline hypohalites, true acetylenic hydrogens are generally replaced by halogen.[1] This reaction has now been applied to vinylacetylene, and the 1-halogen-2-vinylacetylenes whose properties are listed in Table I have been prepared. In a general way they resemble other halogen acetylenes. They are liquids with highly characteristic repulsive sickening odors. Under diminished pressure in an atmosphere of nitrogen they can be distilled, but dangerous explosions occur if air is present, or if heating of the residue is carried too far. A sample of the chloro compound in one instance inflamed spontaneously when a specimen was being removed for analysis.

(1) Straus, Kollek and Heyn, *Ber.*, 63, 1868 (1930).

The compounds when freshly distilled are colorless but they darken on standing and are finally transformed into black, brittle solids. These solids are sensitive to heat and percussion and they explode with considerable violence. The product from the iodo compound is the most sensitive and violent; that from the chloro compound the least.

PHYSICAL PROPERTIES OF $CH_2{=}CH{-}C{\equiv}C{-}X$

Nature of X	B. p., °C.	n^{20}_{D}	d^{20}_{4}	MR_D calcd.	MR_D found	Exaltation
Cl	55 to 57 at 760 mm.	1.4663	1.0032	22.94	23.89	0.95
Br	52 to 53 at 217 mm.	1.5182	1.4804	25.81	26.80	.99
I	78 at 125 mm.	1.5948	1.8968	31.07	31.88	.81

The bromo compound was formed rather rapidly when vinylacetylene was treated with potassium hypobromite; hypochlorite acted very much more slowly and the yields of the chloro compound were rather low. In preparing the iodo compound a solution of iodine in potassium iodide was used. The iodo and bromo compounds have also been obtained[2] by the action of iodine and bromine on di-vinylethynyl-mercury. The iodo compound was also formed when vinylethynylmagnesium bromide was treated with iodine. Since a deficiency of iodine was used, it appears that the tendency of the iodo compound to react with the Grignard reagent is very slight.

In alcoholic solution the iodo compound adds one molecule of hydrogen chloride. This reaction was carried out in the expectation that the product would be the substituted chloroprene, $CH_2{=}CH{-}CCl{=}CHI$. The product did indeed polymerize spontaneously, but it yielded only a sticky black tar and no attempt was made to confirm its structure.

Experimental Part

Preparation of 1-Bromo-2-vinylacetylene.—Bromine (80 g.) was added at 0° to 180 g. of potassium hydroxide in 800 g. of water. Then 30 g. of vinylacetylene was added during one-half hour with stirring under nitrogen. After two hours a heavy oily layer separated. This was dried with calcium chloride and distilled under reduced pressure of nitrogen. Some vinylacetylene was recovered, and then 36.4 g. (55%) of 1-bromo-2-vinylacetylene was collected between 52 and 53° at 217 mm. A small amount of liquid remaining in the distilling flask exploded when further distillation was attempted. The bromovinylacetylene though colorless at first, quickly became yellow and then progressively darker upon standing. Its odor was nauseating and exposure to its vapors caused headaches. A specimen stabilized with hydroquinone did not polymerize within a month. When examined several months later it was a highly explosive black solid.

Anal. Calcd. for C_4H_3Br: C, 36.66; H, 2.27, mol. wt., 130.9. Found: C, 36.72, H, 2.46; mol. wt., 131, 136 (cryoscopic, benzene).

Preparation of 1-Iodo-2-vinylacetylene.—To a solution of 84 g. (1.5 mole) of potassium hydroxide in 1000 g. water at 0°, 65 g. of vinylacetylene was added and then, with vigorous stirring during two hours, a solution of 140 g. of potassium iodide and 127 g. of iodine in 110 cc. of water. After standing overnight, the 1-iodo-2-vinylacetylene (95 g.) which had separated to the bottom was removed, dried with calcium chloride, and distilled under reduced pressure of nitrogen; yield, 49 g. or 27.5%. The compound was at first colorless, but on standing it became reddish-brown. After a month at 10° it had polymerized to a jelly, and after several months to a black solid similar in appearance to charcoal. This polymer was extremely explosive.

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[2] Carothers, Jacobson and Berchet, THIS JOURNAL, 55, 4665 (1933); Vaughn and Nieuwland, *ibid.*, 55, 2150 (1933), report that iodovinylacetylene is obtained from iodine and vinylacetylene in liquid ammonia.

Anal. Calcd. for C_4H_3I: C, 26.97; H, 1.69; mol. wt., 177.95. Found: C, 27.30; H, 1.75; mol. wt., 181 (cryoscopic, benzene).

The iodo compound was also obtained by the action of iodine on vinylethynylmagnesium bromide. To an ethereal solution containing one mole of the reagent, 127 g. (one gram atom) of iodine was slowly added. A smooth reaction occurred and the iodine instantly dissolved with decolorization. A small test sample was removed and found to take up considerably more iodine. However, the main portion was distilled in vacuum and a liquid boiling at 82 to 83° at 150 mm. was collected. This agreed in odor and physical constants with the 1-iodo-2-vinylacetylene described above.

Preparation of 1-Chloro-2-vinylacetylene.—Some difficulty was at first experienced in obtaining this compound, but with the following procedure it was isolated in yields of about 10%. To a solution of 500 g. of potassium hydroxide in 1800 cc. of water at 0° were added 225 g. of chlorine and then 300 g. of vinylacetylene. The mixture was stirred for eight hours. After standing overnight the upper layer (47 g.) was separated, dried with calcium chloride, and distilled under nitrogen. Two distillations gave 23 g. of 1-chloro-2-vinylacetylene boiling at 55 to 57°. It had a nauseating odor and, while colorless at first, it darkened on standing and ultimately polymerized to a black, brittle resinous solid.

Anal. Calcd. for C_4H_3Cl: C, 55.49; H, 3.49; mol. wt., 86.5. Found: C, 55.28; H, 4.06; mol. wt., 87, 89 (cryoscopic, benzene).

Addition of Hydrogen Chloride to 1-Iodo-2-vinylacetylene.—A solution of hydrogen chloride (38 g.) in 95% alcohol was mixed in a pressure bottle with 49 g. of 1-iodo-2-vinylacetylene, 10 g. of ammonium chloride, and 15 g. of cuprous chloride. The bottle was shaken for twenty-four hours at 25° and the oily layer was distilled first with steam and then under nitrogen. The distillate was red in color and boiled at 73.5–74.5° at 35 mm.; yield, 26 g. (44%); d^{20}_4, 1.9161; n^{20}_D 1.6073.

Anal. Calcd. for C_4H_4ICl: C, 22.38; H, 1.88; total silver halide, 0.1704 g., mol. wt., 214.4. Found: C, 22.34; H, 2.07; total silver halide, 0.1699 g.; mol. wt., 225, 228 (cryoscopic, benzene).

Upon standing for several months the compound polymerized to a soft black tar.

The addition of hydrogen chloride to 1-bromo-2-vinylacetylene under similar conditions also gave a volatile product which polymerized on standing.

Summary

The acetylenic hydrogen of vinylacetylene has been replaced by bromine, iodine and chlorine and the corresponding 1-halogen-2-vinylacetylenes obtained. These compounds are unstable liquids which polymerize upon standing to black solid polymers. The latter are explosive when heated or submitted to mechanical shock. Addition of hydrogen chloride to the iodo compound yielded an addition product which also polymerized spontaneously.

WILMINGTON, DELAWARE

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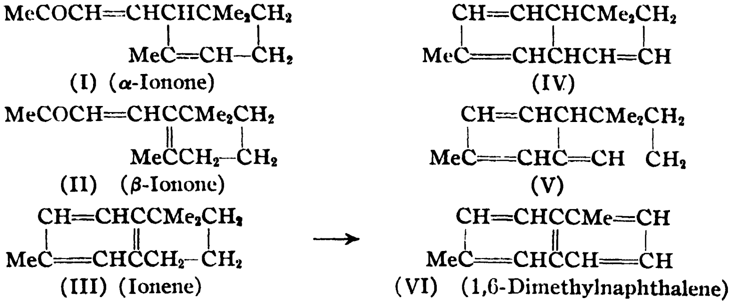
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND THE RESEARCH DEPARTMENT OF THE ASSOCIATED MANUFACTURERS OF TOILET ARTICLES]

The Catalytic Dehydration of Ionone and the Constitution of Ionene[1]

BY MARSTON TAYLOR BOGERT AND VICTOR GEORGE FOURMAN[2]

Tiemann and Krüger,[3] in their classical researches on ionones, $C_{13}H_{20}O$, discovered that when either α-ionone (I), or a mixture of α- and β-ionones, was heated for some time with hydriodic acid, in the presence of small amounts of phosphorus, a molecule of water was split out and a hydrocarbon, $C_{13}H_{18}$, which they christened "ionene," was formed, whose properties they described. Later, Tiemann[4] showed that β-ionone (II), similarly treated, likewise yielded ionene.



$MeCOCH{=}CHCHCMe_2CH_2 / MeC{=}CH{-}CH_2$

(I) (α-Ionone)

$MeCOCH{=}CHCCMe_2CH_2 / MeCCH_2{-}CH_2$

(II) (β-Ionone)

$CH{=}CHCCMe_2CH_2 / MeC{=}CHCCH_2{-}CH_2$

(III) (Ionene)

$CH{=}CHCHCMe_2CH_2 / MeC{=}CHCHCH{=}CH$

(IV)

$CH{=}CHCHCMe_2CH_2 / MeC{=}CHC{=}CH\ CH_2$

(V)

$\longrightarrow$ $CH{=}CHCCMe{=}CH / MeC{=}CHCCH{=}CH$

(VI) (1,6-Dimethylnaphthalene)

Based upon the structure of its oxidation products, Tiemann and Krüger were disposed first to assign to ionene constitution (IV), but finally decided in favor of (V).

Three years later, Barbier and Bouveault[5] proposed formula (III) as the more likely, but cited no new experimental evidence in support of this opinion. Tiemann,[6] in his reply, insisted upon the correctness of his own formula (V). Baeyer and Villiger[7] likewise investigated the constitution of ionene, using their exhaustive bromination method, confirmed the presence of the carbon skeleton common to all three of the suggested formulas, but threw no new light upon the location of the double bonds.

Auwers and Eisenlohr,[8] as the result of their study of the molecular refractivity of ionene, decided in favor of (IV) rather than (V), but apparently failed to consider (III) at all.

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(1) Presented at the Washington Meeting of the American Chemical Society, March 28, 1933, before the Division of Organic Chemistry.

(2) Recently Research Assistant, Research Department, Associated Manufacturers of Toilet Articles; now Chemist for Compagnie Parento, Inc., Croton-on-the-Hudson, New York.

(3) Tiemann and Krüger, (a) *Ber.*, **26**, 2675 (1893); (b) **26**, 2693 (1893); (c) **31**, 808 (1898). Tiemann, (a) British Patent 8763 (May 1, 1893), and (b) 17,539 (Sept. 18, 1893).

(4) Tiemann, *Ber.*, **31**, 873 (1898).

(5) Barbier and Bouveault, *Bull. soc. chim.*, [3] **15**, 1008 (1896).

(6) Tiemann, *Ber.*, **31**, 854 (1898).

(7) Baeyer and Villiger, *ibid.*, **32**, 2429 (1899).

(8) Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **84** 61 (1911).

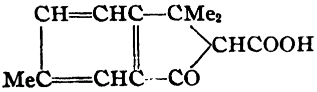
In the course of their researches in the naphthalene field, Ruzicka and Rudolph[9] distilled ionene with sulfur and obtained 1,6-dimethylnaphthalene (VI), using the Barbier and Bouveault formula (III) to explain the reaction. A year later, in his monograph on the sesquiterpenes,[10] Ruzicka accepted the carbon skeleton of ionene as satisfactorily established, but pointed out that the location of the double bonds was still unsettled.

We believe that we have now cleared up this uncertainty, by the experimental work recorded in the present paper, and by the complete synthesis of ionene, preliminary announcement of which appeared a few months ago.[11]

Our interest in the problem was heightened by the recent report of Heilbron, Morton and Webster[12] that when they distilled a vitamin A concentrate with selenium, they obtained 1,6-dimethylnaphthalene (VI) as one of the products, which led them to postulate ionene as an intermediate in this breakdown of the vitamin molecule.

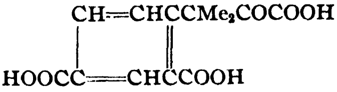
In place of the method used by Tiemann and Krüger,[3] we have found that ionene can be prepared in much larger yield and higher purity by distilling ionone (either α or β) with a small quantity of iodine, a process based upon the observations of Hibbert[13] on the catalytic dehydrating effect of minute amounts of iodine although, so far as we are aware, it has not hitherto been employed for cyclo dehydrations of this type.

Tiemann and Krüger,[3] in their study of the oxidation products of ionene, using chromic acid and potassium permanganate as the oxidizing agents, isolated the 1,1,5-trimethyl-3-indanone-2-carboxylic acid (ionegenogonic acid) (VII), α-keto-β-(2,4-dicarboxyphenyl)-isovaleric acid (ionegenonetricarboxylic acid) (VIII), α-(2-carboxy-4-methylphenyl)-isobutyric acid (ionegenedicarboxylic acid) (IX), and α-(2,4-dicarboxyphenyl)-isobutyric acid (ioniregenetricarboxylic acid) (X). Under the conditions employed by us in oxidizing ionene with potassium permanganate, there were obtained (VIII), (X), and also the β-(2,4-dicarboxyphenyl)-isovaleric acid (XI).



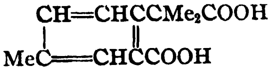
$$\begin{array}{l}\mathrm{CH{=}CHC{-}CMe_2} \\ \qquad\qquad\qquad\quad \rangle\mathrm{CHCOOH} \\ \mathrm{MeC{=}CHC{-}CO}\end{array}$$

(VII)



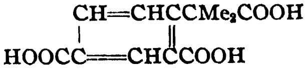
$$\begin{array}{l}\mathrm{CH{=}CHCCMe_2COCOOH} \\ \mathrm{HOOCC{=}CHCCOOH}\end{array}$$

(VIII)



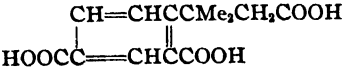
$$\begin{array}{l}\mathrm{CH{=}CHCCMe_2COOH} \\ \mathrm{MeC{=}CHCCOOH}\end{array}$$

(IX)



$$\begin{array}{l}\mathrm{CH{=}CHCCMe_2COOH} \\ \mathrm{HOOCC{=}CHCCOOH}\end{array}$$

(X)



$$\begin{array}{l}\mathrm{CH{=}CHCCMe_2CH_2COOH} \\ \mathrm{HOOCC{=}CHCCOOH}\end{array}$$

(XI)

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(9) Ruzicka and Rudolph, *Helv. Chim. Acta*, **10**, 918 (1927).

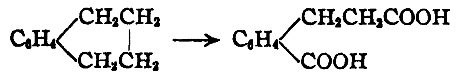
(10) "Ueber Konstitution und Zusammenhänge in der Sesquiterpenreihe," *Fortschr. d. Chem., Phys. u. physik Chem.*, **19**, No. 5, 9 (1928).

(11) Bogert, *Science*, [N. S.] **76**, 475 (1932).

(12) Heilbron, Morton and Webster, *Biochem. J.*, **26**, 1194 (1932).

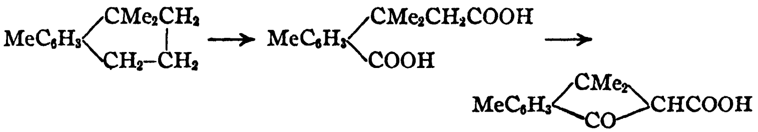
(13) Hibbert, THIS JOURNAL, **37**, 1748 (1915).

All of these compounds are normal oxidation products of an ionene of structure (III). Further, Bamberger and Kitschelt[14] have shown that when tetrahydronaphthalene (tetralin) was oxidized cold by dilute potassium permanganate in acid solution, there was produced the *o*-carboxyhydrocinnamic acid (XII). In other words, the hydroaromatic nucleus opens at the same point in the two cases:



$$C_6H_4\left\langle\begin{array}{l}CH_2CH_2\\ \quad|\\ CH_2CH_2\end{array}\right. \longrightarrow C_6H_4\left\langle\begin{array}{l}CH_2CH_2COOH\\ COOH\end{array}\right.$$

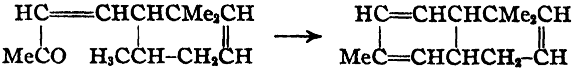
(XII)



$$MeC_6H_3\left\langle\begin{array}{l}CMe_2CH_2\\ \quad|\\ CH_2-CH_2\end{array}\right. \longrightarrow MeC_6H_3\left\langle\begin{array}{l}CMe_2CH_2COOH\\ COOH\end{array}\right. \longrightarrow MeC_6H_3\left\langle\begin{array}{l}CMe_2\\ CO\end{array}\right\rangle CHCOOH$$

(VII)

The formation of such a structure as (III) from β-ionone (II) involves a simple dehydration, exactly similar to that assumed by Tiemann and Krüger[3] in the conversion of the isomeric irone (XIII) into irene (XIV)



$$\begin{array}{l}HC{=\!=}CHCHCMe_2CH\\ \,|\qquad\quad |\qquad\quad \|\\ MeCO\ \ H_3CCH-CH_2CH\end{array} \longrightarrow \begin{array}{l}HC{=}CHCHCMe_2CH\\ \,|\qquad |\qquad\quad \|\\ MeC{=}CHCHCH_2-CH\end{array}$$

(XIII) (XIV)

whereas when α-ionone is the initial material, a shift in the position of one of the olefin bonds must occur during the reaction.

We found it so much more difficult to obtain β-ionone pure and at a price which we could afford, that the ionene used in our experiments was all prepared from α-ionone.

If it be urged that this distillation with iodine has itself shifted the position of the double bond in the ionene first formed, we might point out that such a change would be fully as likely to occur with the concentrated hydriodic acid used by Tiemann and Krüger as the dehydrating agent in their preparation of ionene; and that they obtained the same ionene from α- as from β-ionone.

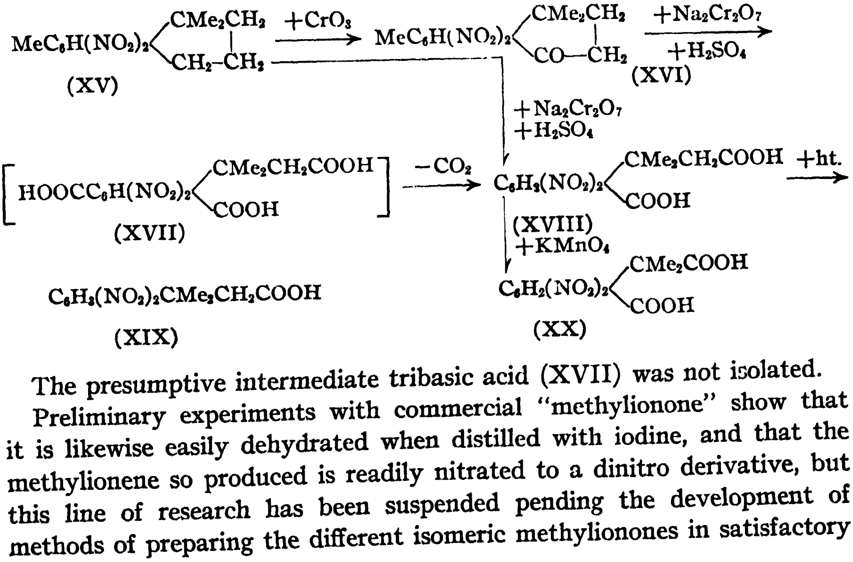
It is pertinent to call attention to the fact that the b. p. of pure ionene is 240–242°, of 1-methylnaphthalene 240–242°, of 2-methylnaphthalene 242° and of tetrahydronaphthalene 206°.

It was the behavior of ionene with nitric and with sulfuric acids which first led us to doubt the correctness of the Tiemann formula (V), and resulted in our reëxamination of the problem, for we found that this hydrocarbon could be easily sulfonated or nitrated. This seemed to us indicative of the presence of a true aromatic nucleus and at variance with the terpene type of structure assumed by Tiemann. He and Krüger noted that ionene dissolved in concentrated sulfuric acid, but did not investigate the reaction or isolate the products. They observed that when irene was treated with fuming nitric acid, there resulted a product with the musky odor of the

(14) Bamberger and Kitschelt, *Ber.*, **23**, 1561 (1890).

polynitrocymenes, but they failed to isolate or identify the products of the reaction, nor did they subject ionene to treatment with nitric acid.

In our own experiments, sulfonation yielded a monosulfo and nitration a dinitro derivative (XV). The position of these groups on the nucleus has not been determined. Reduction of the dinitro formed the nitroamino derivative and not the diamine. Chromic acid oxidized the dinitroionene to a ketone (XVI), which was rearranged to an isomeric form when dissolved in acetic anhydride and treated with a drop of concentrated sulfuric acid. Stronger oxidation of the dinitroionene (XV), or of the ketone (XVI), with dichromate mixture, gave a β-(2-carboxy-dinitrophenyl)-isovaleric acid (XVIII), proving that the two nitro groups were in one and the same ring, *i. e.*, the aromatic cycle. Heating this dicarboxylic acid above its m. p. split out one carbon dioxide with formation of the monocarboxylic acid (XIX). Using acid permanganate solution upon this same dibasic acid (XVIII), oxidized it to the next lower homolog (XX).



$$MeC_6H(NO_2)_2\left<\begin{matrix}CMe_2CH_2\\ |\\ CH_2-CH_2\end{matrix}\right. \xrightarrow{+CrO_3} MeC_6H(NO_2)_2\left<\begin{matrix}CMe_2CH_2\\ |\\ CO-CH_2\end{matrix}\right. \xrightarrow[+H_2SO_4]{+Na_2Cr_2O_7}$$

(XV) (XVI)

$$\xrightarrow[+H_2SO_4]{+Na_2Cr_2O_7}$$

$$\left[HOOCC_6H(NO_2)_2\left<\begin{matrix}CMe_2CH_2COOH\\ COOH\end{matrix}\right.\right] \xrightarrow{-CO_2} C_6H_2(NO_2)_2\left<\begin{matrix}CMe_2CH_2COOH\\ COOH\end{matrix}\right. \xrightarrow{+ht.}$$

(XVII) (XVIII)

$$\xrightarrow{+KMnO_4}$$

$$C_6H_3(NO_2)_2CMe_2CH_2COOH \qquad C_6H_2(NO_2)_2\left<\begin{matrix}CMe_2COOH\\ COOH\end{matrix}\right.$$

(XIX) (XX)

The presumptive intermediate tribasic acid (XVII) was not isolated.

Preliminary experiments with commercial "methylionone" show that it is likewise easily dehydrated when distilled with iodine, and that the methylionene so produced is readily nitrated to a dinitro derivative, but this line of research has been suspended pending the development of methods of preparing the different isomeric methylionones in satisfactory yield and purity.

Further, we suspect that the so-called "irene," obtained by Tiemann and Krüger[3] by dehydration of irone, is identical with ionene, the slight difference in their molecular refractivities being due to the presence of small amounts of impurities, but this investigation also has had to be postponed because of the present high price ($900 per pound) of irone and the lack of convenient methods for its preparation synthetically.

Acknowledgments.—This investigation was made possible by the generous financial support of the Associated Manufacturers of Toilet Articles, notably of Mr. G. A. Pfeiffer, President of Richard Hudnut, Inc.;

and also of the Warren Fund Committee, American Academy of Arts and Sciences. To the courtesy of Mr. A. Doolittle, President of Compagnie Parento, Inc., Croton-on-the-Hudson, N. Y., we are indebted for generous supplies of various ionones; and to Mr. F. Firmenich, President of M. Naef & Co., Geneva, Switzerland, for some very fine specially distilled β-ionone.

Experimental Part

Unless otherwise stated, the melting points recorded in the following pages are all corrected, and were taken by raising the temperature of the bath at the rate of approximately 3° per minute.

α-Ionone (I).—The best grade commercial product was rectified twice, at a pressure of 17 mm., and the fraction boiling at 134–136°, n_D^{20} 1.5041, was used in our experiments. Its *p*-bromophenylhydrazone softened at 134° and melted at 142–143°. Tiemann and Krüger[3] gave the constants for their α-ionone as follows: b. p. at 17 mm., 134–136°, n_D^{20} 1.4980; *p*-bromophenylhydrazone[4,15] softens at 134°, m. p. 142–143°.

Ionene (1,1,6-Trimethyltetralin) (III).—When a mixture of one mole (192 g.) of α-ionone with 1 g. of iodine was heated, the iodine gradually dissolved, and when the temperature of the solution reached about 130°, the evolution of steam began. At 140° the reaction was vigorous at first, but gradually subsided and the distillation was continued until the temperature of the liquid in the flask rose to 250°. The initial distillate consisted almost wholly of the water split out. The crude ionene distilled at 240–245°. It amounted to 140 g., or a yield of 80%, and 12 g. of water was collected. After removal of the water, the crude hydrocarbon was again distilled with 1 g. of iodine and 3 g. more of water was obtained. The ionene which came over was washed with a dilute sodium thiosulfate solution, to free it from traces of iodine, and then with water until colorless. On standing overnight, however, it turned a brownish-red and this color was not removed by washing with thiosulfate solution. Dried over calcium chloride and distilled twice over sodium, a colorless limpid liquid was obtained, b. p. 240–242° at atmospheric pressure; yield 105 g., or 60%. The total water collected was 15 g., or 83%.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.58; H, 10.42. Found: C, 89.40; H, 10.54.

Ionene is a colorless, highly refractive liquid which can be distilled over sodium at atmospheric pressure without apparent decomposition. Tiemann and Krüger[3] reported that their ionene resinified when exposed to the air for a long time, but our product after standing for over a year in contact with the air exhibited no sign of resinification and had only become slightly yellowish.

The constants for the two products are as follows

	Bogert and Fourman	Tiemann and Krüger
B. p. at 10 mm., °C.	107	106–107
B. p. at 14 mm., °C.	114	
B. p. at 752 mm., °C.	240–242	
n_D^{20}	1.5225	1.5244
d^{20}	0.9331	0.9338
d_4^{20}	0.9303	
M_D (Lorentz–Lorenz)	57.13 (56.43)	57.18 (56.43)
EM_D	+0.70	+0.75

Tiemann and Krüger failed to report the yield of ionene obtained by their method, but Ruzicka and Rudolph,[9] on repeating it, obtained a yield of 45% of a product having

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(15) Tiemann, *Ber.*, 28, 1755 (1895)

a boiling point range of 6°. Tiemann and Krüger also found that a glacial acetic acid solution of bromine was decolorized by the addition of their ionene. When this test was applied to our own sample of ionene, hydrobromic acid was evolved and the solution was decolorized.

We had already carried out the distillation of ionene with sulfur, by the method of Vesterberg,[16] and obtained 1,6-dimethylnaphthalene, before we discovered that Ruzicka and Rudolph[9] had done this in 1927. Our results, therefore, present nothing new, except that our yield of the hydrocarbon was slightly better (12% instead of 10%) and the m. p. (113°) of our 1,6-dimethylnaphthalene picrate somewhat higher than theirs (109°). Weissgerber and Kruber[17] recorded the m. p. of this picrate as 114°, and Heilbron, Morton and Webster[12] as 113–114°.

Oxidation of Ionene

Our process of oxidation differed somewhat from that of Tiemann and Krüger,[3] and of Tiemann,[4] and is therefore recorded here.

β-(2,4-Dicarboxyphenyl)-isovaleric Acid (XI).—To a boiling solution of 2 g. of ionene in 100 cc. of water containing a few drops of dilute sodium hydroxide, there was added gradually a solution of 14 g. of potassium permanganate in 300 cc. of hot water and the whole was refluxed for seven hours. The mixture was filtered hot, the filtrate concentrated to about 50 cc. and acidified with dilute hydrochloric acid. The colorless needles which separated carried a mole of water of crystallization and melted, after repeated crystallization from water or dilute alcohol, at 220°; yield, 1.3 g., or 43%.

Anal. Calcd. for $C_{13}H_{16}O_7$: C, 57.72; H, 5.67. Found: C, 57.87; H, 5.58.

Dried to constant weight at 180°, one mole of water was driven off.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, 58.63; H, 5.29 Found: C, 58.33; H, 5.04. Acid equivalent: calculated, 88.7; found, 87.2. *Mol. wt.* Calcd., 266; found, 262.

In the mother liquors from this acid, there was evidence of the presence of a small amount of an acid of lower m. p., probably the **α-(2,4-dicarboxyphenyl)-isobutyric acid (ioniregenetricarboxylic Acid) (X).**—A mixture of 0.1 mole of ionene (17.4 g.), 0.2 g. of sodium hydroxide, 140 g. of potassium permanganate and one liter of water, was refluxed until the solution was colorless (twelve hours), then filtered, the precipitate washed thoroughly with hot water and the combined filtrate and washings evaporated to about 100 cc. and acidified with dilute hydrochloric acid. The crude acid (9.5 g.) which separated was crystallized from water; yield, 7 g., or 28%; m. p. 216.5–218.5°. A sample of the acid recrystallized thrice from water, and which consisted of long colorless needles, m. p. 217°, was analyzed.

Anal. Calcd. for $C_{12}H_{12}O_6$: C, 57.12; H, 4.80. Found: C, 57.45; H, 4.80.

This is evidently the "ioniregenetricarboxylic acid" of Tiemann and Krüger, who found that it lost water at 150°, with formation of an anhydride, m. p. 214°.

Increasing the proportion of the permanganate or the duration of the oxidation gave the same acid (m. p. 217°) in lower yield.

Trimethyl Ester.—Prepared by the action of dry hydrogen chloride upon a solution of the above acid in absolute methyl alcohol, and purified by crystallization first from dilute methyl alcohol and then from hot ethyl alcohol diluted to cloudiness, it formed long colorless needles, m. p. 91°. Tiemann and Krüger recrystallized their methyl ester from ligroin and reported its m. p. as 93°.

Anal. Calcd. for $C_{15}H_{18}O_6$: C, 61.20; H, 6.17. Found: C, 61.29; H, 5.97.

When Tiemann and Krüger heated the silver salt of this acid, they obtained a hydrocarbon which they believed to be isopropylbenzene, but which they failed to identify.

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(16) Vesterberg, *Ber.*, **36**, 4200 (1903).

(17) Weissgerber and Kruber, *ibid.*, **52**, 346 (1919).

As the identification of this hydrocarbon seemed to us to be of importance in establishing the constitution of the parent tricarboxylic acid (X) and thus, indirectly, the structure of ionene itself, we distilled an intimate mixture of the finely ground dry potassium salt (from 18 g. of the acid) with twice its weight of pulverized soda-lime. About 5 g. of hydrocarbon distillate was collected which, after drying over calcium chloride, was redistilled and yielded about 4 g. of a fraction b. p. 140–155° and less than 1 g. of a fraction b. p. 155–160°. The first fraction on rectification gave 3.6 g. boiling at 145–155° (equivalent to a yield of about 40%), most of which came over at 152–153°. The boiling point of isopropylbenzene recorded in the literature is 153°.

This rectified hydrocarbon was heated for thirty minutes at 100° with twice its volume of concentrated sulfuric acid, and the sulfo acid so obtained was then converted into its sulfo chloride and sulfonamide, which latter was crystallized twice from hot alcohol diluted to cloudiness, and then melted at 106°. Mixed with a sample of authentic isopropylbenzene *p*-sulfonamide, prepared from Eastman isopropylbenzene, there was no change in the melting point. The melting point recorded in the literature for this sulfonamide is 107°.

α-Keto-β-(2,4-dicarboxyphenyl)-isovaleric Acid (Ionegenonetricarboxylic Acid) (VIII).—The mother liquors from the preparation of the immediately preceding acid (X) were combined, concentrated to 50 cc. and to the solution more hydrochloric acid was added. Less than 1 g. of crude organic acid was thus obtained from the initial 17.4 g. of ionene. After several crystallizations from water, it appeared in minute colorless needles, which melted at 140–145°, re-solidified at 150°, and then melted at about 206°. These properties coincide with those reported by Tiemann and Krüger[3] for their "ionegenonetricarboxylic acid."

Anal. Calcd. for $C_{13}H_{12}O_7$: % COOH, 48.2; found, 47.7 and 48.0.

Experiments in oxidizing ionene with acid permanganate solutions proved abortive. Part of the ionene was burned to carbon dioxide and the rest was recovered unaltered.

Sulfo Derivatives of Ionene

Ionenesulfonic Acid, $C_{13}H_{17}SO_3H$.—In general, the method was based upon the experience of Hixson and McKee[18] in the sulfonation of cymene, and of Schroeter[19] with tetrahydronaphthalene.

The ionene (17 g.) was first shaken, at room temperature, with an equal volume of concentrated sulfuric acid, to free it from possible traces of unsaturated contaminants. The ionene layer was then separated, mixed with an equal volume of fresh concentrated sulfuric acid, and the mixture stirred vigorously at 90° for two hours. After standing overnight at room temperature, it was poured into 200 cc. of water and ice, the solution made faintly alkaline with dilute sodium hydroxide, heated to boiling and about 50 g. of salt (sodium chloride) added. The sodium sulfonate which separated was crystallized from 150 cc. of water half saturated with sodium chloride; yield, 18 g., or 50%. The sample analyzed was recrystallized thrice more from small volumes of water, and then formed colorless needles which carried five moles of water of crystallization, which was driven off at 180°.

Anal. Calcd. for $C_{13}H_{17}SO_3Na \cdot 5H_2O$: H_2O, 24.60. Found: 24.90.

Anal. Calcd. for $C_{13}H_{17}SO_3Na$: C, 56.48; H, 6.21. Found: C, 56.58; H, 6.73.

The free sulfonic acid was very easily soluble in water.

Barium Salt.—This separated in colorless glistening plates, when a solution of barium chloride was added to one of the sodium sulfonate. It crystallized from water with three moles of water of crystallization.

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(18) Hixson and McKee, *Ind. Eng. Chem.*, **10**, 982 (1918).

(19) Schroeter, *Ann.*, **426**, 1–160 (1922).

Anal. Calcd. for $(C_{13}H_{17}SO_3)_2Ba\cdot3H_2O$: H_2O, 7.7. Found: 7.3.

Anal. Calcd. for $(C_{13}H_{17}SO_3)_2Ba$: C, 48.46; H, 5.32; $BaSO_4$, 36.25. Found: C, 48.39; H, 5.11; $BaSO_4$, 36.82.

Sulfochloride.—Prepared from the anhydrous sodium sulfonate and phosphorus pentachloride, the crude product was purified by solution in benzene and addition of petroleum ether, which precipitated small amounts of tar. After a repetition of this purification, the benzene solution was evaporated and the residue crystallized from ligroin. Small colorless crystals resulted, m. p. 89°; yield, 1.7 g. from 2.5 g. of sodium sulfonate, or 70%.

Anal. Calcd. for $C_{13}H_{17}SO_2Cl$: C, 57.24; H, 6.27. Found: C, 57.28; H, 6.31.

Sulfonamide.—When the sulfochloride was digested with concentrated ammonium hydroxide solution and the crude product recrystallized thrice from 50% alcohol, this sulfonamide was obtained in colorless lustrous plates, m. p. 157–158°; yield from 1 g. of sulfochloride, 0.7 g. or 75%.

Anal. Calcd. for $C_{13}H_{19}O_2NS$: C, 61.61; H, 7.57. Found: C, 61.74; H, 7.71.

Variations in the temperature (30–110°) or duration of the heating of the ionene–sulfuric acid mixture, made no change in the product, as evidenced by the m. p. of the sulfochlorides and sulfonamides prepared therefrom. The position of the sulfo group in the nucleus has not been determined.

Schroeter[19] obtained the 2-sulfo acid when he sulfonated tetrahydronaphthalene with concentrated sulfuric acid, and a mixture of the 1- and 2-sulfo acids when he used chlorosulfonic acid. He found that the barium salt of the 1-acid crystallized with three moles of water, whereas the barium salt of the 2-acid crystallized water-free.

Nitration of Ionene

Dinitroionene (XV).—In the course of ninety minutes, 40 g. of ionene was introduced, drop by drop and with vigorous stirring, into 150 cc. of nitric acid (sp. gr., 1.5) containing 30 g. of phosphorus pentoxide, keeping the flask in an ice-pack. After all the ionene had been added, and without removing the flask from the ice-pack, the stirring was continued for a further half hour and the flask left at the same temperature for several hours longer, after which its contents were poured into 1500 cc. of water and ice, the precipitated nitro derivative filtered out, washed with water and crystallized from alcohol; yield, 45 g., or 70%. Further purification was accomplished by recrystallization from hot alcohol diluted to cloudiness, glacial acetic acid, benzene or boiling concentrated nitric acid. The pure compound formed pale yellowish plates, m. p. 103°; yield, 38 g., or 58%.

Anal. Calcd. for $C_{13}H_{16}O_4N_2$: C, 59.06; H, 6.11; N, 10.61. Found: C, 58.97; H, 6.18; N, 10.72.

The above method is based upon that used by Behrend and Roth[20] in the nitration of β-pentacetylglucose. The same product was secured when the nitration was conducted in the presence of concentrated sulfuric acid, instead of phosphorus pentoxide, but the yields were not as good. No trace of an isomeric dinitro derivative was detected in these nitration experiments, but there was formed, as a by-product, a small amount of a red oil, which may have contained a mononitro derivative, but from which no pure compound could be isolated.

Schroeter,[19] in his study of the nitration of tetrahydronaphthalene with a mixture of nitric and sulfuric acids, obtained a eutectic mixture of the 1,2- and 1,3-dinitro derivatives, the former of which could be further nitrated (to the 1,2,4-trinitro derivative), but not the latter. All attempts to introduce a third nitro group into our dinitroionene

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(20) Behrend and Roth, *Ann.*, **331**, 381 (1904).

proved fruitless, and the fact that this dinitro derivative is unchanged by boiling concentrated nitric acid is scarcely in accord with the assumption of any terpene type formula for ionene.

The location of these two nitro groups on the aromatic nucleus was not determined. It seems most likely that they will be found to be ortho to the methyl group, *i. e.*, on either side of it, which would make them meta to each other.

Nitroaminoionene.—A solution of 2 g. of dinitroionene in 200 cc. of ethyl alcohol was reduced in an Adams hydrogenator, in the presence of 0.1 g. of platinum oxide catalyst.[21] The hydrogen was absorbed rapidly at the outset, but this rate fell quickly during the first ten minutes, and at the end of an hour and a half the reduction was complete. The catalyst was removed and the alcoholic solution concentrated. As the solution cooled, the nitroamine crystallized in canary-yellow needles, m. p. 166.5°. Purified through the hydrochloride, and then crystallized from alcohol, it melted at 171°; yield, 1.4 g., or 80%.

Anal. Calcd. for $C_{13}H_{18}O_2N_2$: C, 66.62; H, 7.75. Found: C, 66.78; H, 7.78.

Hydrochloride.—The amine was dissolved in dilute hydrochloric acid, the solution warmed gently and concentrated hydrochloric acid added until crystallization began. These colorless crystals were removed, washed with concentrated hydrochloric acid, redissolved in dilute hydrochloric acid, reprecipitated by the concentrated acid, filtered out and dried in a desiccator. They were partially hydrolyzed by cold water or even on standing exposed to air and moisture. Heated at the rate of 4° per minute, the salt decomposed at 237–239°. Addition of dilute ammonium hydroxide to a dilute aqueous solution of the salt, liberated the free base.

Acetyl Derivative.—Prepared from the nitroamine and acetic anhydride and purified by crystallization from 60% ethyl alcohol, it formed colorless needles, m. p. 158°; yield, 75–80%.

Anal. Calcd. for $C_{15}H_{20}O_3N_2$: C, 65.17; H, 7.30. Found: C, 65.07; H, 7.68.

Attempts were made to reduce the dinitro or nitroamino derivative of ionene to the diamine, either catalytically, or with the aid of stannous chloride, tin and hydrochloric acid, phenylhydrazine or other reducing agents. All failed. When the dinitro derivative was the initial material, the only reduction product was the nitroamine. When the latter was the initial material, there was usually no reaction short of total decomposition.

Oxidation of Dinitroionene

α-Dinitroionenone (XVI).—To a suspension of 15 g. of dinitroionene in a mixture of 400 cc. of glacial acetic and 60 g. of concentrated sulfuric acid, there was added gradually, in the course of two hours, 10 g. of chromium trioxide with vigorous stirring, keeping the mixture at first in an ice-pack and then allowing it to warm to room temperature. Upon the completion of the oxidation, the mixture was poured into water, the precipitate removed, washed with water until the washings were colorless and then crystallized from alcohol. There was thus obtained 9 g. of very pale yellow needles, m. p. 157°. From the mother liquor 2 g. additional was recovered, making a total yield of 11 g., or 70%.

Anal. Calcd. for $C_{13}H_{14}O_5N_2$: C, 56.09; H, 5.07; N, 10.07. Found: C, 56.23, 55.79; H, 5.02, 4.97; N, 10.38. *Mol. wt.* (borneol, Rast): calcd., 278; found, 266.

The product was insoluble in sodium hydroxide or in hydrochloric acid. It dissolved in cold concentrated sulfuric acid and reprecipitated unaltered when this solution was poured upon ice. An alcoholic solution was colored wine-red by the addition of dilute sodium hydroxide. Under similar treatment, an acetone solution turned brown,

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(21) Adams, "Organic Syntheses," John Wiley and Sons. Inc., New York, 1932, Coll. Vol. I. p. 452.

but no indigo derivative was formed, an evidence that the compound was not an *o*-nitrobenzaldehyde. It did not reduce an ammoniacal silver nitrate solution in the cold, nor dilute permanganate when heated with its acetone solution.

Oxime.—When a solution of 1.4 g. of the above ketone in 10 cc. of alcohol was refluxed for fifteen minutes with a molar equivalent of hydroxylamine hydrochloride and three of sodium hydroxide, and the mixture then poured into ice and dilute hydrochloric acid, a pale brown precipitate separated, which was collected, washed with water and crystallized repeatedly from alcohol, when it formed colorless needles, m. p. 188.5°; yield 1.1 g., or 74%.

Anal. Calcd. for $C_{13}H_{15}O_6N_3$: C, 53.28; H, 5.16; N, 14.34. Found: C, 53.39; H, 4.87; N, 14.57.

The compound was insoluble in dilute hydrochloric acid. In dilute sodium hydroxide it dissolved and the sodium salt of the oxime crystallized in bright yellow needles which decomposed at about 125°.

No oxime was formed when sodium carbonate was used instead of sodium hydroxide upon the mixture of ketone and hydroxylamine, even after refluxing for three hours, the initial ketone being recovered unchanged.

β-Dinitroionenone.—After adding one drop of concentrated sulfuric acid to a solution of 4 g. of α-dinitroionenone in 15 cc. of acetic anhydride, the solution was refluxed for an hour and left overnight at room temperature. The acetic anhydride was then distilled off under diminished pressure and the residue, as it cooled, solidified. This solid was washed with petroleum ether and crystallized, first from hot acetic acid diluted to cloudiness, and then from alcohol, when it appeared in small pale yellow needles, m. p. 99°; yield, 3.5 g., or 87%.

Anal. Calcd. for $C_{13}H_{14}O_6N_2$: C, 56.09; H, 5.07; N, 10.07. Found: C, 56.39, 56.21; H, 4.86, 4.90; N, 10.06. *Mol. wt.* (borneol, Rast): calcd., 278; found, 268.

When this product (1 g.) was dissolved in concentrated sulfuric acid (5 cc.) and the solution poured upon ice, a solid separated which, when washed with water and crystallized from alcohol, proved to be the α-isomer (m. p. 157°), as shown by a mixed melting point and by its other properties. The addition of either dilute or concentrated hydrochloric acid to an alcoholic solution of the β isomer caused no change. Isomerization of the β to the α form was also accomplished by adding several drops of dilute sodium hydroxide to a solution of the β form (1 g.) in alcohol (5 cc.), when the solution turned red and the product which crystallized out proved to be the α isomer. One isomer could not be converted into the other by heating above its melting point, nor by seeding the molten material with crystals of its isomer. Without the addition of the drop of concentrated sulfuric acid, acetic anhydride was powerless to rearrange the α to the β isomer. It might be mentioned also that had this dinitroionenone been an aldehyde and not a ketone, the treatment with acetic anhydride and sulfuric acid should have yielded the aldehyde diacetate.

Oxidation of Dinitroionene and of Dinitroionenone

β-(2-Carboxy-dinitrophenyl)-isovaleric Acid (XVIII).—A solution of 5 g. of dinitroionene in 150 g. of glacial acetic acid and 75 cc. of concentrated sulfuric acid was refluxed for an hour, while a solution of 30 g. of $Na_2Cr_2O_7.2H_2O$ in 60 cc. of water was added dropwise. After standing overnight at room temperature the mixture was poured into ice water, the precipitate filtered out, washed with water until the washings were colorless, dissolved in dilute sodium hydroxide solution, filtered and the filtrate acidified with dilute hydrochloric acid. The precipitated acid was crystallized thrice from water, 100 parts of which at 100° dissolved 1.6 parts of the acid; yield, 3.4 g., or 54%. The purified acid formed yellow needles, carrying one mole of water of crystallization. At 150°, the acid melted with elimination of this water of crystallization, resolidified and melted then at 177°.

Anal. Calcd. for $C_{12}H_{14}O_9N_2$: C, 43.62; H, 4.27; N, 8.49. Found: C, 43.49; H, 4.40; N, 8.74. *Acid equivalent.* Calcd., 165; found, 168.

This same acid was obtained by similarly oxidizing dinitroionenone (α or β form) in glacial acetic acid solution with sodium dichromate and concentrated sulfuric acid.

β-Dinitrophenyl-isovaleric Acid (XIX).—The above dicarboxylic acid (XVIII) was kept at a temperature just above its melting point as long as carbon dioxide was evolved. The melt was allowed to resolidify and was then dissolved in alcohol, the solution filtered, and the filtrate diluted with water until crystallization began. Recrystallized from water, it formed pale yellowish needles, m. p. 166.5–168.5°; yield, 1.5 g. from 2.5 g. of initial dicarboxylic acid, or 74%. It was very easily soluble in alcohol, but much less soluble in water than its antecedent dicarboxylic acid.

Anal. Calcd. for $C_{11}H_{10}O_6N_2$: C, 49.24; H, 4.51. Found: C, 48.81; H, 4.74.

α-(2-Carboxydinitrophenyl)-isobutyric Acid (XX).—A solution of 2.5 g. of the corresponding isovaleric acid (XVIII) in 250 cc. of water, 5 cc. of concentrated sulfuric acid and 0.7 g. of potassium permanganate, was refluxed until the color of the solution was discharged (forty minutes). The manganese dioxide precipitated was filtered out, washed thoroughly with hot water, and the combined washings and filtrate concentrated. The colorless needles which separated were dissolved in dilute sodium hydroxide, the solution filtered and the filtrate precipitated by the addition of dilute hydrochloric acid. After crystallization twice from water, the product melted at 170.5°; yield, 1.9 g., or 84%. Its solubility was about 1.3 parts in 100 parts of water at 100°.

Anal. Calcd. for $C_{11}H_{10}O_8N_2$: C, 44.28; H, 3.38. Found: C, 44.47; H, 3.63.

Summary

1. Ionene is conveniently prepared, in excellent yield, by the distillation of α- or β-ionone with small amounts of iodine.

2. That ionene is a true 1,1,6-trimethyltetralin is evidenced by its smooth sulfonation and nitration, and by the oxidation products obtained from ionene itself and from its dinitro derivative.

3. Dinitroionenone can be obtained in two isomeric forms which are mutually interconvertible.

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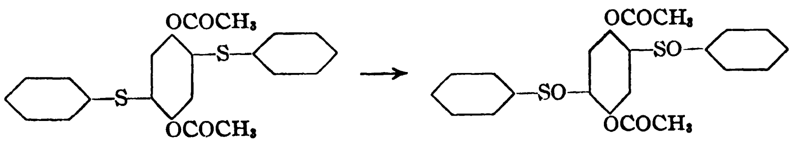
[Contribution from the Chemical Laboratory of the University of Illinois]

Diastereoisomers of 2,5-Diphenylsulfinylhydroquinone Diacetate

By Marion E. Maclean[1] and Roger Adams

Phillips[2] in 1925 first demonstrated that a sulfur atom in combination with three dissimilar groups could be resolved. His investigations[3] involved the preparation of optically active sulfinic esters and of sulfoxides. Bell and Bennett[4] and their associates extended the study to the isomerism of aliphatic and aliphatic–aromatic disulfoxides and to cyclic di- and trisulfoxides. These authors are confident that the semi-polar linkage between oxygen and sulfur is an important factor in producing asymmetry. Others[5] urge caution in adopting this as an official explanation. Bergmann[6] on the other hand opposes the idea of a semi-polar bond and believes the resolution due to the fact that the oxygen atom lies in a different plane from that of the bonds holding the other two groups to the sulfur atom and states that all the cases given can be explained on this basis.

An additional pair of stereoisomers among the disulfoxides is described in this communication. It is the first example of such isomerism in a di-diarylsulfoxide. A meso and a racemic form of 2,5-diphenylsulfinyl-1,4-hydroquinone diacetate (II) were obtained by oxidizing the corresponding disulfide (I) with hydrogen peroxide. The α- and β-disulfoxides differ in m. p. by approximately 30° and are markedly different in solubility. They have strikingly different crystalline forms. Both the α and β forms are readily reduced to the parent disulfide and oxidized to the same disulfone. In the preparation of the disulfoxides a small amount of monosulfoxide was always produced.



I II

Experimental

α- and β-2,5-Diphenylsulfinylhydroquinone-1,4-diacetates (II).—To a suspension

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(1) The junior author held during 1931–32 the Julia C. G. Piatt fellowship awarded by the A. A. U. W. She desires to express her thanks for this aid.

(2) Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

(3) Harrison, Kenyon and Phillips, *ibid.*, 2079 (1926); Clarke, Kenyon and Phillips, *ibid.*, 188 (1927); Holloway, Kenyon and Phillips, 3000 (1928); Kenyon and Phillips, *ibid.*, 1676 (1930).

(4) Bell and Bennett, *ibid.*, 1798 (1927); 86, 3189 (1928); 15 (1929); 1 (1930); Bell and Waddington, *ibid.*, 2832 (1929); Bell, Mosses and Statham, *ibid.*, 1668 (1930); Bennett and Statham, *ibid.*, 1684, 1690 (1931); Bennett and Waddington, *ibid.*, 1692 (1931).

(5) Sidgwick, "Electronic Theory of Valency," Oxford-Clarendon Press, 1927; deVries and Rodebush, This Journal, **53**, 2888 (1931).

(6) Bergmann, Engel and Sandor, *Z. physik. Chem.*, **B10**, 397 (1930); Bergmann and Tschudnowsky, *Ber.*, **65**, 457 (1932).

of 24 g. of diphenylthiohydroquinone diacetate[7] (I) in 750 cc. of glacial acetic acid was added 12.5 cc. of perhydrol and with mechanical stirring, the mixture left for five days. An additional 100 cc. of glacial acetic acid was added after three days. About 5 g. of solid (the disulfide) still remaining after five days was filtered off.

The filtrate was diluted with about 2 liters of water. On settling, 12.6 g. of a pale cream solid was obtained (Part A).

A large amount of water added to the filtrate from Part A gave 4.9 g. (Part B).

The total yield, calculating as disulfoxide and correcting for the disulfide recovered, was 83%. (A.) Three grams of (A) was digested with 200 cc. of carbon tetrachloride to remove impurities. The residue, 1.9 g., was dissolved in 130 cc. of 95% alcohol and gave 1.65 g. of colorless plates which melted with decomposition at 207–208°[8] (corr.), with signs of decomposition from 179°.

Anal. (α-form, m. p. 207–208°) Calcd. for $C_{22}H_{18}O_6S_2$: C, 59.73; H, 4.07; S, 14.48. Found: C, 60.26; H, 4.16; S, 14.50.

On evaporation of the carbon tetrachloride solution, a solid was obtained which was purified from alcohol, m. p. 142.5–145.5°[8] with softening at 140° (corr.). This on analysis proved to be a monosulfoxide.

Anal. (Compound m. p. 142.5–145.5°) Calcd. for $C_{22}H_{18}O_5S_2$: C, 61.97; H, 4.23; S, 15.02. Found: C, 61.98; H, 4.28; S, 14.93.

(B) A solution of 2.5 g. of (B) in 60 cc. of alcohol, on cooling gave 1.6 g. of short, colorless crystals, melting 173.5–175° (corr.) to a dark red liquid with darkening from 166°. Recrystallization did not change the melting point.

Anal. (β-form, m. p. 173.5–175°) Calcd. for $C_{22}H_{18}O_6S_2$: C, 59.73; H, 4.07; S, 14.48. Found: C, 60.48; H, 4.16; S, 14.27.

Mixed melting points of various proportions of the α- and β-disulfoxides were determined. In every case the mixture melted over a range intermediate between the melting points of the separate α- and β-forms.

Repetition of the isolation of α- and β-forms on a larger scale gave essentially the same results except that the presence of a larger amount of the monosulfoxide rendered the separation more difficult.

2,5-Diphenylsulfonylhydroquinone Diacetate from α-Disulfoxide.—To a solution of 2 g. of the α-disulfoxide in 50 cc. of glacial acetic acid was added 5 cc. of perhydrol. Upon heating overnight on the steam-bath under reflux, a large quantity of small crystals deposited. After about twenty-six hours the crystals were filtered from the still hot solution and washed with a little glacial acetic acid, then alcohol. The precipitate weighed 1.2 g. A part was recrystallized from dioxane and part from glacial acetic acid. Both solutions were violet by reflected light. The recrystallized compound melted when pure with decomposition at 270–271°, darkening beginning about 220°.

Anal. Calcd. for $C_{22}H_{18}O_8S_2$: C, 55.69; H, 3.79; S, 13.50. Found: C, 55.37; H, 3.99; S, 13.67.

A similar reaction with the β-disulfoxide gave the same compound.

2,5-Diphenylthiohydroquinone Diacetate by Reduction of α-2,5-Diphenylsulfinylhydroquinone Diacetate.—To a solution of 1 g. of α-disulfoxide in 40 cc. of glacial acetic acid, 5 g. of zinc dust was added, and the mixture refluxed for seventeen hours. The solution was filtered hot into about 200 cc. of water. The slightly gummy precipitate which settled after about two hours was filtered and recrystallized from alcohol. The product showed exactly the same slender needle form and melting point as 2,5-diphenylthiohydroquinone diacetate. The identity was confirmed by a mixed melting point.

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[7] Posner, *Ann.*, **336**, 134 (1904).

[8] The exact m. p. of the α- and the β-forms varied with the rate of heating and the temperature of the bath when samples were inserted. But samples of the two, melted simultaneously, always showed a difference such as that indicated here.

In a similar way the β-form was also reduced to 2,5-diphenylthiohydroquinone.

Summary

The meso and racemic forms of 2,5-diphenylsulfinylhydroquinone have been isolated. These represent a pair of diastereoisomers in the class of di-diarylsulfoxides.

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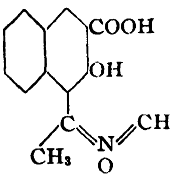
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Study of Certain Analogs of Resolvable Diphenyls

BY MARION E. MACLEAN[1] AND ROGER ADAMS

The cause of optical activity in properly substituted diphenyls is now generally ascribed to restricted rotation of the two rings.[2] Meisenheimer[3] has observed in certain substituted oximes (I) and Mills[4] in certain nitronaphthalenes (II) and quinoline derivatives (III), optical isomerism which may also be explained on the basis of restricted rotation due to the interference of groups.



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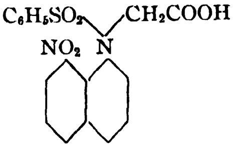

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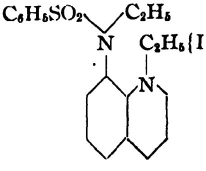

III

Similar possibilities[5] in substituted aryl aliphatic compounds have been suggested but none have as yet been prepared in which resolution has been realized.

It is clear from the work cited above that other cases of optical activity caused by interference of adjacent groups are to be anticipated. Compounds related to the diphenyl series of the general structure indicated in IV, V and VI have now been investigated.

From experience in the diphenyl series, the methyl group may be assumed to be relatively large.[2] Consequently, if (a) in the above formulas represents a methyl group, the 2,2′ groups in these molecules should pro-

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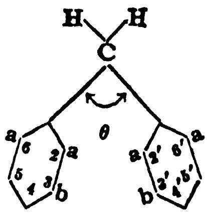
(1) Submitted as part of a thesis for the degree of Doctor of Philosophy at the University of Illinois. The junior author held during 1931–1932 the Julia C. G. Piatt Memorial Fellowship of the A. A. U. W. She desires to express her thanks for this aid.

(2) Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

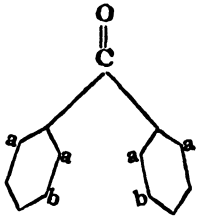
(3) Meisenheimer, Theilacker and Beisswenger, *Ann.*, **495**, 249 (1932).

(4) Mills, *Trans. Faraday Soc.*, **26**, 431 (1930); Mills and Breckenridge, *J. Chem. Soc.*, 2209 (1932); Mills and Elliott, *ibid.*, 1291 (1928).

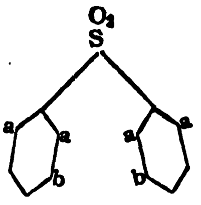
(5) Hyde and Adams, THIS JOURNAL, **50**, 2499 (1928); Maxwell and Adams, *ibid.*, **52**, 2959 (1930)



IV



V



VI

duce a pronounced interference and thus lead to non-coplanar rings which would make possible optical isomerism, provided (1) that the angle θ which in an undistorted carbon atom is 109° 28′ is not materially modified by the substituent groups and (2) that the two rings during rotation on the methylene groups are not so synchronized as to slip by each other.

Strong evidence that the valence angles of a carbon atom vary with the character of the atoms or groups attached has been offered by Ingold,[6] Thorpe and others.

Dipole moment measurements have also indicated in some instances spreading of the valence angles. The very small moment of diphenylmethane[7] led to the conclusion that the axes of the two phenyl groups are very nearly in a straight line. In benzophenone and its *p*-substituted products, the angle between the single valencies has been found to be about 130°.[8] For diphenyl sulfone, however, the valence angles of sulfur have been calculated as practically 109°.[9] It is possible that in the dimesityl compounds the deformation would be greater than in the corresponding diphenylmethane derivatives.

From these data it might be predicted that in dimesitylmethane and dimesityl ketone, the methane carbon would be so distorted that the 2,2′-methyl groups would interfere only slightly if at all and restricted rotation with consequent optical activity might not result. Restricted rotation would seem more likely in the case of dimesitylsulfone, although the length of the carbon-to-sulfur linkage might be enough greater than the carbon-to-methylene linkage to govern to some extent the possibility of interference between the methyl groups.

A compound of each type mentioned above has been prepared, 3,3′-diaminodimesitylmethane (VII), 3,3′-diaminodimesityl ketone (VIII) and 3,3′-diaminodimesityl sulfone (IX).

Each compound yielded a crystalline di-camphor sulfonate and di-bromocamphor sulfonate, but these on fractional crystallization gave no evidence of separation into diastereoisomers and on decomposition with ammonia

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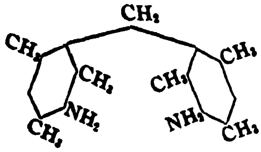
(6) Ingold, *J. Chem. Soc.*, **119**, 305 (1921), and subsequent papers by the same author and his co-workers.

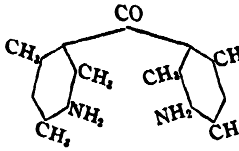
(7) Estermann, *Z. physik. Chem.*, **B1**, 161 (1928).

(8) Bergmann, Engel and Meyer, *Ber.*, **65**, 446 (1932).

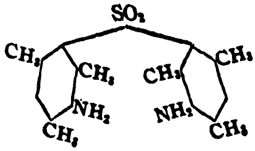
(9) Bergmann and Tschudnowsky, *ibid.*, **65**, 457 (1932).



VII



VIII



IX

at 0°, each salt yielded an inactive amino compound. No mutarotation of the salts was observed even at 0°. This failure to demonstrate the presence of enantiomorphs in the three diamino compounds suggests a distortion of the tetrahedral structure of the sulfur and of the methane carbon atoms in these compounds to a degree which permits free rotation of the mesityl groups or perhaps a synchronizing of the rings during rotation, or even both.

Experimental

Dimesityl ketone was prepared either by the action of carbon monoxide on mesitylene under pressure in the presence of aluminum chloride[10] or by the condensation of 2,4,6-trimethylbenzoyl chloride and mesitylene. Upon nitration and reduction, VIII was obtained. To prove that nitration did not yield a 3,5-dinitro instead of a 3,3′-dinitro derivative, 3,5-dinitromesityl mesityl ketone was prepared from 3,5-dinitro-2,4,6-trimethylbenzoyl chloride and mesitylene and was shown not to be identical with the nitration product of dimesityl ketone.

3,3′-Diaminodimesitylmethane was obtained by a Clemmensen reduction of the dinitrodimesityl ketone. Attempts to nitrate dimesitylmethane prepared from formaldehyde and mesitylene proved unsuccessful.

Diaminodimesityl sulfone was obtained by nitration and reduction of dimesityl sulfone. By analogy to the ketone, it was assumed that the nitro groups entered one in each ring.

Dimesityl Sulfone.—A mixture of 147 g. of mesitylene sulfonyl chloride,[11] 100 g. of mesitylene and 1 liter of carbon disulfide was placed in a three-necked, 1-liter, round-bottomed flask fitted with a reflux condenser protected by a drying tube and 100 g. of aluminum chloride was added, causing an immediate mild reaction. Refluxing on a water-bath was maintained for eleven hours. The carbon disulfide was distilled off and the contents of the flask poured out onto ice. The product, after filtering and drying, weighed 153 g. (75%). Purification is best accomplished by crystallization from glacial acetic acid, m. p. 202–204° (corr.). This substance has been described previously by Meyer,[12] who reported m. p. 195° but gave no details for the preparation.

3,3′-Dinitrodimesityl Sulfone.—A mixture of 9.5 g. of dimesitylsulfone and 1 liter of concentrated nitric acid (sp. gr. 1.42) was heated in an open, round-bottomed flask on the steam-bath for five hours. The dimesitylsulfone dissolved to a pale yellow solution. Upon cooling, 9 g. of very pale yellow crystals separated and more could be recovered by diluting the filtrate, m. p. 172–174° (corr.). This proved to be the pure product. Less pure portions were recrystallized from glacial acetic acid.

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[10] Krase and Macmillan prepared this product by the high pressure reaction and kindly furnished a sample for part of the experiments described in this investigation.

[11] Demény, *Rec. trav. chim.*, **50**, 51 (1931).

[12] Meyer, *Ann.*, **433**, 327 (1923).

Anal. Calcd. for $C_{18}H_{20}N_2O_6S$: N, 7.14. Found: N, 7.37, 7.30.

3,3'-Diaminodimesityl Sulfone.—A mixture of 17.2 g. of crude 3,3'-dinitrodimesityl sulfone, 500 cc. of glacial acetic acid, 150 cc. of water and 35 cc. of concentrated hydrochloric acid in a three-necked flask provided with a mercury-sealed stirrer and a reflux condenser was heated on a steam cone for a short time until the solid had dissolved completely. Powdered zinc was added in portions, 90 g. in all, and 20 cc. of water with 15 cc. of concentrated hydrochloric acid was also added after a time. The heating was continued for about nineteen hours.

After filtration, the amine was precipitated from the acetic acid solution, previously cooled and diluted with ice, by addition of excess ammonia. It was further purified by redissolving in warm dilute hydrochloric acid and reprecipitating with ammonia (yield 13.2 g., 91%). After one recrystallization from glacial acetic acid and one from alcohol the needles had a m. p. of 217.5–218.5° (corr.).

Anal. Calcd. for $C_{18}H_{24}N_2O_2S$: C, 65.02; H, 7.28; N, 8.43. Found: C, 65.31; H, 7.63; N, 8.51.

Dimesityl Ketone.—This product was made by the Friedel and Crafts reaction as described by Kohler and Baltzly.[13] It had the same melting point as that obtained by the action of carbon dioxide on mesitylene.[10]

3,3'-Dinitrodimesityl Ketone.—A solution of 70.5 g. of crude dimesityl ketone in a liter of concentrated sulfuric acid was cooled to −14.5°. Then 35.5 g. of nitric acid (sp. gr. 1.5) in 250 cc. of concentrated sulfuric acid, also previously cooled in an ice–salt bath, was added slowly with mechanical stirring over a period of two hours. The temperature did not rise above −9.5° during the addition but remained below −10° nearly the entire time. Stirring was continued and the solution was left standing for three hours, the temperature rising nearly to 0°. Then the liquid was poured very slowly, with vigorous stirring, onto ice; yield, 89 g. (95%). The nearly white, granular crystals were purified by recrystallization from alcohol, m. p. 171.5–172.5° (corr.).

Anal. Calcd. for $C_{19}H_{20}N_2O_5$: C, 64.01; H, 5.66; N, 7.86. Found: C, 64.15; H, 5.77; N, 7.87.

3,3'-Diaminodimesityl Ketone.—In 650 cc. of glacial acetic acid 39.8 g. of 3,3'-dinitrodimesityl ketone was suspended, then 130 cc. of water and 35 cc. of concentrated hydrochloric acid were added. It was not found necessary to have the nitro compound completely in solution. With mechanical stirring, zinc dust was added in small portions over a period of four hours, 125 g. in all. The mixture was not allowed to heat appreciably. After all the zinc dust had been added, the stirring was continued for twelve hours. After filtering and washing with acetic acid, the filtrate was cooled with ice and excess of ammonia was slowly added with stirring. The solution should not be allowed to heat during neutralization since this caused contamination with a gummy substance. The amine was dissolved in dilute hydrochloric acid and reprecipitated with excess ammonia; yield 30 g. (91%). It was purified by recrystallization from 50% alcohol, forming yellow needles, m. p. 163–164.5° (corr.).

Anal. Calcd. for $C_{19}H_{24}N_2O$: C, 76.98; H, 8.17; N, 9.46. Found: C, 77.14; H, 8.36; N, 9.40.

3,3'-Diaminodimesitylmethane.—To the zinc amalgam (prepared from 100 g. of zinc) and 30 g. of 3,3'-diaminodimesityl ketone dilute hydrochloric acid (about 1:2) was added and the mixture refluxed approximately twelve hours. From time to time more

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(13) Kohler and Baltzly, THIS JOURNAL, **54**, 4023 (1932).

concentrated acid was added. At the end of this period the yellow diaminodimesityl ketone had entirely dissolved.

The colorless solution was filtered from the remaining amalgam, diluted with ice, and excess ammonia added gradually, avoiding a rise in temperature. The solid was dissolved in hydrochloric acid and reprecipitated; yield, 26 g. (91%). The product was recrystallized from alcohol, m. p. 160–160.5° (corr.).

Anal. Calcd. for $C_{19}H_{26}N_2$: C, 80.79; H, 9.28; N, 9.92. Found: C, 81.10; H, 9.32; N, 11.31.

It will be noted that there is a peculiar discrepancy between the results of the combustions and the nitrogen analyses, although several analyses gave the same results, indicating the compound to be perfectly homogeneous in composition. The hydrochloride of the compound was prepared to be analyzed for chlorine.

Preparation of the Dihydrochloride.—To a suspension of 1 g. of diaminodimesityl methane in about 30 cc. of water, hydrochloric acid was added dropwise. The material first dissolved then a white precipitate formed. On boiling, this dissolved but did not reprecipitate on cooling. The compound was precipitated with concentrated hydrochloric acid, filtered and washed with dilute hydrochloric acid; decomposition about 220–290°. After redissolving and reprecipitating, the melting point was unchanged.

Anal. Calcd. for $C_{19}H_{26}N_2 \cdot 2HCl$: Cl, 19.97. Found: Cl, 19.84.

There would seem to be little question that the compound *is* 3,3′-diaminodimesitylmethane, although no explanation is seen for the anomalous nitrogen analyses.

3,5-Dinitrodimesityl Ketone.—To 10 g. of crude 3,5-dinitro-2,4,6-trimethylbenzoyl chloride[14] and 25 g. of mesitylene, 5 g. of aluminum chloride was added. After mechanical stirring for four days at room temperature, the mixture was heated to 70° for a short time, then decomposed with ice and hydrochloric acid. The solid product was extracted with benzene, the solution filtered from a small amount of sticky solid, and the benzene and excess mesitylene removed with steam. The yellow solid remaining was dissolved in a mixture of 400 cc. of alcohol and 70 cc. of acetone. On cooling, yellow crystals separated. After two further recrystallizations from glacial acetic acid the melting point was constant at 199–200° (corr.).

A mixture of this compound with 3,3′-dinitrodimesityl ketone (prepared by nitration of dimesityl ketone) melted at 149–180°.

Anal. Calcd. for $C_{10}H_{20}N_2O_5$: C, 64.01; H, 5.66; N, 7.86. Found: C, 65.05; H, 5.96; N, 7.74.

Dimesitylmethane.—A mixture of 160 g. of mesitylene and 50 g. of formalin was stirred mechanically and cooled to 0°. Dry hydrogen chloride was passed in rapidly until the solution was saturated. After one and one-half hours powdered zinc chloride was added in small portions, 120 g. in all.

After the reaction had proceeded for about twelve hours, the adhering liquid was filtered off. The solid was boiled with water, cooled, crushed and filtered. It was further treated with concentrated hydrochloric acid, washed, then treated with concentrated ammonia, to remove all excess zinc chloride; yield, 130 g. (77.5%). The compound was purified by vacuum distillation, then crystallization from glacial acetic acid, as colorless crystals, m. p. 133–134° (corr.). Kohler and Baltzly[13] report m. p. 135°.

Attempts to Resolve VII, VIII and IX.—The di-camphor sulfonic acid and dibromocamphor sulfonic acid salts of 3,3′-diaminodimesityl sulfone and 3,3′-diaminodimesityl ketone were prepared in absolute ethyl acetate and sufficient absolute ethyl or methyl alcohol then added to clear the solution. The analogous salts of 3,3′-diamino-

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(14) Kunckell and Hildebrandt, *Ber.*, **34**, 1826 (1901).

dimesitylmethane were made in water. Various fractions obtained by evaporation gave the same rotation and the recrystallized product of each also the same rotation.

TABLE I

ROTATIONS OF SALTS OF VII, VIII AND IX

	3,3'-Diamino-dimesityl	Salt, camphor sulfonic, I; bromocamphor sulfonic, II	0.1000 g. made up to cc.	Solvent, abs.	Temp., °C.	α_D	$[\alpha]_D$
1	Sulfone	I	$10:l = 1$	Alcohol	20	+0.34	+34
2	Sulfone	II	$20:l = 1$	Methanol	27	+ .26	+52
3	Ketone	I	$20:l = 2$	Alcohol	25	+ .28	+25
4	Ketone	II	$20:l = 2$	Methanol	26	+ .58	+58
5	Methane	I	$20:l = 2$	Methanol	28	+ .23	+23
6	Methane	II	$20:l = 1$	Methanol	30[a]	+ .29	+58

	Formula	Analyses, % Calcd.	Analyses, % Found
1	$C_{38}H_{52}N_2O_8S_3$	N, 3.68	3.74
2	$C_{38}H_{50}Br_2N_2O_8S_3$[a,b]	Br, 17.40	16.08
3	$C_{39}H_{52}N_2O_7S_2\cdot 2H_2O$[c]	C, 61.54; H, 7.43;	61.37; 7.71
		N, 3.68; S, 8.42	3.68; 8.79
4	$C_{39}H_{50}Br_2N_2O_7S_2\cdot 2H_2O$[c]	C, 50.95; H, 5.92	50.94; 6.12
		N, 3.05; S, 6.98	3.32; 6.75
5	$C_{39}H_{54}N_2O_6S_2$	N, 3.94	4.43
6	$C_{39}H_{52}Br_2N_2S_2O_6$	N, 3.22	3.58

[a] The salt was hygroscopic, which made impossible satisfactory determinations of water of hydration. [b] The analysis indicates a hydrated salt. [c] Solution prepared at 0°.

Summary

The 3,3'-diamino derivatives of dimesitylmethane, dimesityl ketone and dimesityl sulfone have been prepared. Attempts to resolve them resulted in failure.

A discussion is given of the theoretical possibilities in compounds of this type.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Labilities or Electronegativities of Some Unsaturated Alkyl Radicals as Determined by Hydrogen Chloride Scission of Organolead Compounds

BY HENRY GILMAN, EDMUND B. TOWNE AND H. L. JONES

Introduction

The scission of phenylfuryl-, phenylthienyl- and furylthienyl-lead compounds by hydrogen chloride has been advanced in support of the super-aromaticity of furan.[1] In order to test the validity of such evidence it appeared desirable to establish the relative labilities of some other unsaturated radicals, particularly of the aliphatic series.

On the basis of a significant amount of experimental data, it appeared altogether reasonable to expect that in accordance with the following general reaction

$$(\text{Aryl})_3\text{Pb}(\text{Alkyl}) + \text{HCl} \longrightarrow (\text{Aryl})_2\text{Pb}(\text{Cl})(\text{Alkyl}) + \text{Aryl H} \qquad (\text{I})$$

a mixed organolead compound containing aryl and alkyl groups would be cleaved by hydrogen chloride to give an aromatic but not an aliphatic hydrocarbon. However, Austin[2a] has shown that when an alcoholic solution of triphenylallyllead is heated with hydrobromic acid, triphenyllead bromide is formed in practically quantitative yields

$$(C_6H_5)_3PbC_3H_5 + HBr \longrightarrow (C_6H_5)_3PbBr \qquad (\text{II})$$

This splitting reaction is at variance with what might have been expected on the assumption that the allyl radical is a weakly electronegative group.[2b]

Inasmuch as cleavage of R_4Pb compounds by hydrogen chloride in chloroform or benzene proceeds quite smoothly, and inasmuch as these conditions were used in the aromaticity studies, we treated a chloroform solution of triphenylallyllead with hydrogen chloride. The yield of phenyllead halides (triphenyllead chloride and diphenyllead dichloride) was about 95%, and propene was identified. The formation of propene as a cleavage product is significant, for it shows that the allyl group as such was cleaved and that at least a part of the allyl groups did not undergo addition of hydrogen chloride at the olefinic linkage prior to cleavage. Even if hydrogen chloride added first to the olefinic linkage, the splitting would still have been anomalous, according to some interpretations, in the sense that an aliphatic radical, in this case a chloropropyl group, would have been cleaved prior to an aryl or phenyl group.

Comparison of Cleavage of Organolead with Other Organometallic Compounds.—The unexpected splitting products of triphenylallyllead suggested that cleavage of organolead compounds might possibly be unlike that of other organometallic compounds, particularly the unsymmetrical organomercurials which have been so satisfactorily studied by Kharasch and co-workers.[3] In order to supplement early work, the splitting of a miscellany of mixed R_4Pb compounds by hydrogen chloride was investigated. The results indicate that the decreasing order of lability of the radicals, with hydrogen chloride as the cleavage agent, is as follows: $\alpha\text{-}C_{10}H_7\text{-} > C_6H_5\text{-} > C_6H_5CH_2\text{-}$. This order, together with that established for the α-furyl and α-thienyl radicals as well as for many alkyl radicals, indicates that the radicals conform rather closely with the order established by the hydrogen chloride cleavage of other organometallic compounds.

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[1] Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932). This article contains references to earlier studies on the cleavage of organolead compounds by hydrogen chloride.

[2] (a) Austin, THIS JOURNAL, **53**, 3514 (1931); (b) "Annual Survey of American Chemistry," 1931, Vol. VI, p. 210.

It should be stated that orienting cleavage experiments with diphenyldibiphenyllead and triphenylbiphenyllead gave both diphenyl and benzene as splitting products with the former in slight excess. Orienting experiments with diphenyl-di-*p*-dimethylaminophenyllead, $(C_6H_5)_2Pb[C_6H_4N(CH_3)_2]_2$, and with triphenyl-*p*-dimethylaminophenyllead, were more conclusive and showed definitely that the *p*-dimethylaminophenyl radical is cleaved more rapidly than the phenyl radical. This is as one would have predicted, both on the basis of so-called relative electronegativities and relative aromaticities.

Cleavage of Unsaturated Radicals Other than Allyl.—Having shown that R_4Pb compounds might be used generally to determine the relative labilities of radicals, it was of interest to learn whether the allyl radical was peculiar in the sense that it alone among unsaturated alkyl radicals was cleaved prior to an aromatic radical. First, the cleavage of triphenyl-β-styryllead was effected in chloroform by hydrogen chloride. The yield of phenyllead chlorides was 96% and styrene was identified.

$$(C_6H_5)_3PbCH{=}CHC_6H_5 + HCl \longrightarrow (C_6H_5)_3PbCl + C_6H_5CH{=}CH_2 \quad \text{(III)}$$

Here, also, an unsaturated radical is removed prior to an aryl group. Second, the scission of triphenyl-3-butenyllead under corresponding conditions gave diphenyl-3-butenyllead chloride and benzene

$$(C_6H_5)_3PbCH_2CH_2CH{=}CH_2 + HCl \longrightarrow (C_6H_5)_2Pb(Cl)(CH_2CH_2CH{=}CH_2) + C_6H_6 \quad \text{(IV)}$$

From this reaction it follows that the 3-butenyl radical, unlike the allyl and β-styryl radicals, is less labile than the phenyl radical. The order of decreasing labilities on the basis of hydrogen chloride cleavage of mixed organolead compounds is

$$[CH_2{=}CHCH_2\text{—} \text{ and } C_6H_5CH{=}CH\text{—}] > C_6H_5\text{—} > C_2H_5\text{—} > CH_2{=}CHCH_2CH_2\text{—}$$

The ethyl radical was shown to be more labile than the 3-butenyl radical by the formation of ethane and ethyl-3-butenyllead dichloride from the cleavage of triethyl-3-butenyllead. Other studies indicate that the

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(3) Kharasch and Flenner, THIS JOURNAL, 54, 674 (1932). Other references to the extensive studies by Kharasch and co-workers are contained in this most recent paper. In addition a critical survey is presented of the splitting of other organometallic compounds.

phenylacetenyl radical ($C_6H_5C\equiv C-$) is more labile and the 4-pentenyl radical ($CH_2=CHCH_2CH_2CH_2-$) is less labile than the phenyl radical.

If one might generalize from these restricted observations with unsaturated alkyl radicals, it appears that unsaturated radicals vary significantly in their relative labilities, depending on the position of the unsaturated linkage with respect to the carbon–metal bond and on the nature of substituents in the unsaturated radical. It seems probable that different types of unsaturated radicals might form a series related to that of aryl and saturated alkyl groups. The preferential cleavage of $C_6H_5C\equiv C-$ and $C_6H_5CH=CH-$ indicates that α,β-unsaturation with lead may be a significant factor in the greater labilities of some unsaturated radicals. If this be the case, it raises a question on the structure of triphenylallyllead. We may have in this compound a $CH_3CH=CH-$ and not a $CH_2=CH-CH_2-$ linkage. This remains to be determined.

The results with the allyl and β-styryl radicals appear to be at variance with some conclusions on relative aromaticities drawn from a series of relative labilities as measured by rates of hydrogen chloride cleavage.[1] However, the allyl and styryl radicals do have some physical and chemical characteristics which might warrant a formal if not a compelling analogy with aromatic types. Admittedly, that particular evidence for the super-aromaticity of furan based on organometallic cleavage is apparently impaired by the present findings.

Experimental Part

The point of departure for most of the syntheses was tetraphenyllead,[4a] and directions for its preparation have been improved so that the yield has reached 80%. Triphenyllead chloride and diphenyllead dichloride were prepared by standard procedures;[4b] and the method of analysis for lead was that described earlier.[4c] Details of the cleavage of $R^1_2PbR^2_2$ and $R^1_3PbR^2$ types have already been given,[1] and the same general procedure was followed in the experiments to be described.

Triphenylallyllead.—The yield of triphenylallyllead[2a] from triphenyllead chloride and allylmagnesium bromide was 82.4%. Five cleavage experiments were carried out with hydrogen chloride, using chloroform as the solvent. The runs varied from 0.01 to 0.02 mole; the temperature from 26 to 50°; and the time of reaction from forty-five minutes to two hours. Triphenyllead chloride was identified by the method of mixed melting points. Diphenyllead dichloride was converted, by means of phenylmagnesium bromide, to tetraphenyllead. The yield of phenyllead halides (composed of the soluble triphenyllead chloride and the insoluble diphenyllead dichloride) averaged about 95%. In a typical cleavage the yield of diphenyllead dichloride was 17.4%, and the yield of triphenyllead chloride was 77.6%. Cleavage was generally carried slightly beyond the R_3PbCl stage and to the R_2PbCl_2 stage in order to avoid contamination with R_4Pb compound. The propene was characterized by conversion to 1,2-dibromopropane.

Triphenyl-3-butenyllead.—3-Buten-1-ol ($CH_2=CHCH_2CH_2OH$) was prepared by the addition of gaseous formaldehyde to a magnesium-free ethereal solution of allylmagnesium bromide. The formaldehyde was added until the absence of the color test showed the Grignard reagent to be used up. The yield of crude 3-buten-1-ol, based on allylmagnesium bromide, was 59%; and rectification by distillation gave a 43% yield.

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[4] (a) THIS JOURNAL, **49**, 2315 (1927); (b) *ibid.*, **51**, 3112 (1929); (c) *ibid.*, **50**, 1714 (1928).

3-Butenyl bromide ($CH_2{=}CHCH_2CH_2Br$) was prepared in accordance with the directions of Juvala[5] from the alcohol, phosphorus tribromide and pyridine.

3-Butenylmagnesium bromide was prepared in practically a quantitative yield under standard conditions,[6] the yield being determined by titration. This Grignard reagent was prepared previously by a less direct method, from 1,2,4-tribromobutane and magnesium in ether.[7] In order to characterize our RMgBr compound, it was carbonated to give allylacetic acid ($CH_2{=}CHCH_2CH_2COOH$), and this in turn was characterized by the preparation of 3,4-dibromovaleric acid[8] by means of bromine in carbon tetrachloride.

Triphenyl-3-butenyllead was prepared by adding the Grignard reagent to a suspension of triphenyllead chloride in ether. The yield of crude product, based on triphenyllead chloride, was 96%. Purification was effected from petroleum ether (b. p. 30–80°) to give a white solid melting at 84–86°.

Anal. Calcd. for $C_{22}H_{22}Pb$: Pb, 42.01. Found: Pb, 41.78 and 41.87.

The triphenyl-3-butenyllead in chloroform was treated with dry hydrogen chloride in the customary manner, the solution being kept at 40–45°. After thirty minutes a flocculent white precipitate formed. From the chloroform there was isolated diphenyl-3-butenyllead chloride [see Reaction (IV)] which melted with decomposition at 134–135° when recrystallized from alcohol.

Anal. Calcd. for $C_{16}H_{17}ClPb$: Cl, 7.85. Found: Cl, 7.72 and 7.79.

The diphenyl-3-butenyllead chloride was characterized by treatment with phenylmagnesium bromide, which converted it to the known triphenyl-3-butenyllead (mixed melting point determination). There was no evidence of any significant cleavage to give butene. However, benzene was identified as a product of cleavage, the yield of *m*-dinitrobenzene (mixed m. p.) being 42%. Another scission product appears to be phenyl-3-butenyllead dichloride formed in about one-half the quantity of diphenyl-3-butenyllead chloride. The instability of this R_2PbCl_2 compound is remindful of di-2-thienyllead dichloride.[1]

Triethyl-3-butenyllead, $(C_2H_5)_3PbCH_2CH_2CH{=}CH_2$.—The triethyl-3-butenyllead was prepared from triethyllead chloride and 3-butenylmagnesium bromide. The yield of crude material was 81%, and this on fractionation gave a 63% yield of product distilling at 78° (3 mm.); d_4^{20} 1.5616; n_D^{20} 1.5230.

Anal. Calcd. for $C_{10}H_{22}Pb$: Pb, 59.34. Found: Pb, 59.10.

Cleavage with hydrogen chloride was effected separately in ether, in chloroform and in benzene solutions. The same products were obtained from each medium. The yield of ethyl-3-butenyllead dichloride, from benzene, was 82%.

Anal. Calcd. for $C_6H_{12}Cl_2Pb$: Cl, 19.58. Found: Cl, 19.70.

Ethane was identified as the other product of cleavage, and no significant quantity of butene was contained in the ethane.

Triphenyl-β-styryllead.—Triphenyllead chloride was added to a filtered ether solution of β-styrylmagnesium bromide which was obtained in 77% yield. The yield of triphenyl-β-styryllead, melting at 107–109°, after crystallization from alcohol, was 28%. In addition, the usual amount of 1,4-diphenylbutadiene (from coupling during the Grignard reaction) was obtained, as well as a small quantity of tetraphenyllead.

Anal. Calcd. for $C_{26}H_{22}Pb$: Pb, 38.26. Found: Pb, 38.11 and 37.97.

Cleavage was effected in warm chloroform solution, the flask being swept out by a

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(5) Juvala, *Ber.*, **63**, 1989 (1930).

(6) THIS JOURNAL, **51**, 1576 (1929).

(7) V. Braun and Deutsch, *Ber.*, **44**, 3699 (1911).

(8) Messerschmidt, *Ann.*, **208**, 100 (1881).

stream of dry nitrogen prior to the admission of hydrogen chloride. The yield of diphenyllead dichloride was 16.2% and this was identified as tetraphenyllead subsequent to treatment with phenylmagnesium bromide. The yield of triphenyllead chloride (mixed m. p.) was 80.17%, making a total yield of phenyllead halides of 96.37%. Styrene was isolated and identified.

Triphenyl-α-naphthyllead.—This compound was prepared in a customary manner by adding α-naphthylmagnesium bromide to triphenyllead chloride. The yield was 66% of a compound which when recrystallized from alcohol melted at 131°.[9]

Anal. Calcd. for $C_{28}H_{22}Pb$: Pb, 36.66. Found: Pb, 36.57 and 36.70.

Scission of a chloroform solution gave a 62.5% yield of naphthalene.

Diphenyl-di-α-naphthyllead.—The yield of this compound from diphenyllead dichloride and α-naphthylmagnesium bromide was 81.2%, and after crystallization from alcohol it melted at 196–197°.[9] Hydrogen chloride cleavage in benzene gave 93% of diphenyllead dichloride and 88.2% of naphthalene.

Triphenylbenzyllead.—Slightly more than one equivalent of benzylmagnesium chloride was necessary to give a positive color test in the reaction with triphenyllead chloride. The yield of triphenylbenzyllead[10] melting at 91° after crystallization from alcohol was 89%.

Anal. Calcd. for $C_{25}H_{22}Pb$: Pb, 39.33. Found: Pb, 38.94 and 38.86.

Cleavage of a boiling chloroform solution gave some unaltered triphenylbenzyllead, lead chloride and diphenylbenzyllead chloride which sinters at 157°.

Anal. Calcd. for $C_{19}H_{17}ClPb$: Pb, 42.48. Found: Pb, 42.25 and 41.80.

Cleavage in petroleum ether (b. p. 50–60°) gave a 76% yield of pure diphenylbenzyllead chloride and an 86% yield of benzene as determined by the weight of *m*-dinitrobenzene.

Summary

1. In connection with relative aromaticities, a study has been made of the rates of cleavage of unsymmetrical organolead compounds by means of hydrogen chloride.

2. The relative order of labilities or so-called electronegativities of radicals is essentially that observed in the scission reactions of other organometallic compounds by hydrogen chloride: [α-C_4H_3S– and α-$C_{10}H_7$–] > C_6H_5– > [C_2H_5– and $C_6H_5CH_2$–].

3. Triphenylallyllead gives triphenyllead chloride and propene, indicating (contrary to expectations) that the allyl group is more labile than the phenyl group. Likewise, the β-styryl group is cleaved before phenyl. However, the phenyl radical is removed before the 3-butenyl radical. Accordingly, it appears that the unsaturated radicals can form a series the members of which are more or less labile than the phenyl radical depending on the position of the unsaturated linkage and the nature of substituents in the unsaturated alkyl group. Also, the results appear to be at variance with some concepts of relative aromaticities, particularly as they concern furan.

AMES, IOWA

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[9] Krause and Schmitz, *Ber.*, **52**, 2150 (1919).

[10] Krause and Schlöttig, *ibid.*, **63**, 1384 (1930).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Preparation of Some Derivatives of Triphenylgermanium by Means of Sodium Triphenylgermanide

BY CHARLES A. KRAUS AND CLARENCE S. SHERMAN[1]

Two general methods are available for coupling organic groups to atoms of amphoteric elements. The first, and most common, is to treat a halogen derivative of the element in question with the Grignard reagent containing the organic group. The second method, which, incidentally, was the method originally employed in the preparation of metallo-organic compounds, is to treat an alkali-metal alloy of the amphoteric element with a halide of the desired organic group. Thus tetraethyllead may conveniently be prepared either by treating lead chloride with ethylmagnesium bromide or by treating a sodium–lead alloy with ethyl bromide. In making organic derivatives of fourth group elements containing a number of different organic groups, two methods are similarly available. Thus, triphenylethylgermanium has been prepared by the action of ethylmagnesium bromide on triphenylgermanium bromide[2] and by the action of ethyl bromide on sodium triphenylgermanide.[3] In both cases the coupling occurs as a result of the splitting off of bromine as bromide. The Grignard reagent is ordinarily the more convenient, but the second method, if it is applicable, generally gives the better yields, in fact it is usually quantitative. In some syntheses the second method is applicable when the first is not. This is particularly true of reactions in which atoms of amphoteric elements are to be coupled to one another. Thus, Kraus and Greer[4] have built up chains containing as many as five tin atoms.

The second method becomes more difficult of application as the atomic number of the amphoteric element diminishes. In the case of silicon, it is not ordinarily possible to prepare the necessary sodium compounds.[5] In the case of the triphenylgermanium group, the salt $NaGe(C_6H_5)_3$ is readily prepared in liquid ammonia solution and reactions with many organic halides take place readily and often quantitatively.[6] We have prepared a number of mono-alkyl triphenylgermanes and have coupled the triphenylgermanium and triethylgermanium groups to form the mixed digermane according to the reaction equation

$$(C_6H_5)_3GeNa + (C_2H_5)_3GeBr = (C_6H_5)_3Ge—Ge(C_2H_5)_3 + NaBr \qquad (1)$$

Experimental

The apparatus and procedure employed is much the same as that of Kraus and Nutting.[6] Triphenylgermanium (hexaphenyldigermane) is treated with an equivalent amount of sodium in liquid ammonia and the organic halide is added, usually in slight excess. It is necessary to exclude oxygen since sodium triphenylgermanide is readily oxidized. When the reaction is completed, the ammonia is evaporated and the residue is extracted with a suitable solvent.

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(1) Rice Fellow in Chemistry at Brown University.

(2) Orndorff, Tabern and Dennis, THIS JOURNAL, **49**, 2512 (1927).

(3) Kraus and Nutting, *ibid.*, **54**, 1622 (1932).

(4) Kraus and Greer, *ibid.*, **47**, 2568 (1925).

(5) Walter K. Nelson, Thesis, Brown University, 1930.

(6) Kraus and Nutting, THIS JOURNAL, **54**, 1622 (1932).

***n*-Propyltriphenylgermanium.**—Approximately 4.5 g. of triphenylgermanium was converted to the sodium salt in liquid ammonia and a slight excess of *n*-propyl bromide was added by means of a stream of ammonia vapor as described by Kraus and Nutting. The end-point of the reaction was indicated by the disappearance of the yellow color characteristic of the sodium salt. After evaporating the ammonia, the contents of the tube were treated with boiling water. The sodium bromide dissolved while the *n*-propyltriphenylgermanium melted and collected as a liquid in the bottom of the tube. The material, when cold, was thrown on a filter and, after drying in air, was extracted with isopropyl alcohol. After concentrating the alcohol solution, needle crystals of *n*-propyltriphenylgermanium were obtained, melting at 85.5–86.5°. A sample of the material, dissolved in chloroform and precipitated by addition of methyl alcohol, melted at 86.0–86.5°. Another sample, sublimed *in vacuo* at 100°, also melted at 86.0–86.5°.

The compound was analyzed for germanium according to the method commonly employed in this Laboratory by oxidizing with fuming sulfuric and nitric acids. The precautions pointed out by Kraus and Flood[7] were found very helpful.

Anal. Subs., 0.2122, 0.2630: GeO_2, 0.0645, 0.0798. Calcd. for $C_3H_7Ge(C_6H_5)_3$: Ge, 20.96. Ge found: Ge, 21.09, 21.06.

n-Propyltriphenylgermanium is very soluble in chloroform, benzene, petroleum ether, and trichloroethylene. It is slightly soluble in isopropyl alcohol and almost insoluble in methyl alcohol. It is insoluble in liquid ammonia and does not react with sodium in that solvent.

***n*-Butyltriphenylgermanium.**—Approximately 1.2 g. of triphenylgermanium was reduced to the sodium salt and then treated with *n*-butyl bromide. After evaporating the ammonia, the product was treated with boiling water, the resulting material was filtered and dried in a vacuum desiccator over phosphorus pentoxide. The product was finally extracted with isopropyl alcohol and recrystallized from the same solvent, m. p. 84.5–85.5°.

Anal. Subs., 0.3216, 0.2534: GeO_2, 0.0939, 0.0742. Calcd. for $C_4H_9Ge(C_6H_5)_3$: Ge, 20.15. Ge found: Ge, 20.26, 20.32.

n-Butyltriphenylgermanium is very soluble in petroleum ether, benzene, chloroform, trichloroethylene and ether. It is slightly soluble in isopropyl alcohol and practically insoluble in methyl alcohol. From isopropyl alcohol, it crystallizes in the form of long, colorless needles.

***n*-Amyltriphenylgermanium.**—Sodium triphenylgermanide was treated with *n*-amyl bromide as in the previous preparation. After evaporating the ammonia and treating with boiling water, an oily liquid was obtained which solidified only on cooling with a salt–ice mixture. The solution was filtered cold and the mass on the filter paper was dried in a vacuum desiccator over phosphorus pentoxide. It was extracted with isopropyl alcohol. On evaporating the alcohol, an oil separated which crystallized on standing overnight. The material was purified by sublimation at 90°, the condensing surface being cooled by boiling ammonia; m. p. 42–43°.

Anal. Subs., 0.3519, 0.1905: GeO_2, 0.0989, 0.0535. Calcd. for $C_5H_{11}Ge(C_6H_5)_3$: Ge, 19.38. Ge found: Ge, 19.50, 19.49.

n-Amyltriphenylgermanium is exceedingly soluble in benzene, isopropyl alcohol, petroleum ether and trichloroethylene, and fairly soluble in methyl alcohol, from which

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(7) Kraus and Flood, THIS JOURNAL, 54, 1637 (1932).

solvent it separates in the form of soft, plate-like crystals which are colorless and odorless. It is best recrystallized from that solvent and is most readily purified by sublimation *in vacuo*.

Benzyltriphenylgermanium.—Sodium triphenylgermanide was treated with benzyl chloride, the benzyl chloride being added to the ammonia solution of the salt by means of a special funnel. This procedure was necessary because benzyl chloride ammonolyzes very readily. After evaporating the ammonia, the product was treated with boiling water and the oil which separated was allowed to solidify, after which it was thrown on a filter, dried, and extracted with isopropyl alcohol. It was recrystallized from the same solvent. From a cool solution it slowly crystallized in the form of long, thin, plate-like crystals, m. p. 82.5–83.5°.

Anal. Subs., 0.2103, 0.2185: GeO_2, 0.0558, 0.0580. Calcd. for $C_6H_5CH_2Ge(C_6H_5)_3$: Ge, 18.39. Ge found: Ge, 18.41, 18.42.

Benzyltriphenylgermanium is very soluble in benzene, petroleum ether and chloroform. It is sparingly soluble in isopropyl alcohol and almost insoluble in methyl alcohol. It is best recrystallized from a 50–50 mixture of isopropyl and methyl alcohols.

Triphenylgermanyltriethylgermanium.—This compound was prepared according to reaction (1). This reaction cannot be carried out in liquid ammonia because triethylgermanium bromide is ammonolyzed in that solvent. The reaction may, however, be carried out in a neutral solvent such as benzene in which sodium triphenylgermanide is slightly soluble. The sodium triphenylgermanide is prepared in the usual way in liquid ammonia.

Approximately 1.8 g. of triphenylgermanium was treated with an equivalent quantity of sodium in liquid ammonia. After evaporating the ammonia, the tube was exhausted at room temperature for thirty-six hours, when the pressure had fallen to 0.01 mm. About 20 cc. of dry benzene was distilled into the reaction tube and a slight excess of triethylgermanium bromide was added from a pipet.

The color of the benzene solution, which was originally a deep brown, lightened as reaction proceeded. The tube was allowed to stand for three hours, being shaken at intervals in order to mix the contents. The tube was then heated to the boiling point and the contents thrown on a filter while hot. The benzene solution was concentrated and, upon cooling, fine crystals separated. The last traces of benzene were removed under diminished pressure and the crystals thus obtained were washed with methyl alcohol. The material was then crystallized from absolute ethyl alcohol. From this solvent, fairly large and definite rhombic crystals were obtained which, after several recrystallizations, retained only a trace of brown color. They had the odor characteristic of triethylgermanium compounds.

Anal. Subs., 0.3001, 0.2946: GeO_2, 0.1350, 0.1330. Calcd. for $(C_6H_5)_3Ge\text{-}Ge(C_2H_5)_3$: Ge, 31.34. Found: Ge, 31.22, 31.33.

Triphenylgermanyltriethylgermanium is extremely soluble in benzene and chloroform. It is soluble in trichloroethylene, petroleum ether, ethyl alcohol and isopropyl alcohol and sparingly soluble in methyl alcohol. It is best recrystallized from absolute ethyl alcohol from which it separates in the form of well-defined rhombic crystals. It melts at 89.5–90.5° and is stable in air. On crystallization from benzene, the compound retains benzene of crystallization.

Summary

n-Propyl-, *n*-butyl-, *n*-amyl- and benzyltriphenylgermanium have been prepared by the action of the corresponding alkyl halides on sodium triphenylgermanide in liquid ammonia solution.

Triphenylgermanyltriethylgermanium, $(C_6H_5)_3Ge-Ge(C_2H_5)_3$, has been prepared by the action of triethylgermanium bromide on sodium triphenylgermanide in benzene solution.

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The Reactivity of Atoms and Groups in Organic Compounds. XIV. The Influence of Substituents on the Thermal Stability of Certain Derivatives of Malonic Acid

BY JAMES F. NORRIS AND HELEN F. TUCKER[1]

It has been shown in this Laboratory[2] that the substitution products of malonic acid begin to lose carbon dioxide at different temperatures and that there is a relationship between these temperatures and the radicals present in the acids. The results indicated the relative effects of the several radicals on the lability toward heat of a carbon to carbon bond in compounds of this type. Other investigations have shown that the rates vary at which these acids decompose in solutions at a fixed temperature and with change of solvent.[3,4,5,6] Hinshelwood[7] has studied the effect of temperature on the rate at which solid malonic acid decomposes.

As it seemed probable that an extension of the work would lead to results of value in interpreting pyrolytic reactions in general, a large number of compounds were studied.

Some time after the appearance of the paper by Norris and Young and when further work was in progress in this Laboratory, Marshall[8] reported a repetition, with slightly modified apparatus, of the published work and the results obtained by him in the study of some additional compounds. With the exception of two acids, which will be considered later in this paper, the temperatures checked within three degrees or less those given in the earlier papers.

The results published from this Laboratory were obtained by heating the acid in a tube connected with a long capillary tube, which contained a bead of mercury. The temperature of the acid was raised at the rate of one degree per minute and the position of the bead and the temperatures noted. The results were plotted and a line drawn through the points. The

(1) From the thesis of Helen F. Tucker presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1933.

(2) Norris and Young, THIS JOURNAL, **52**, 5066 (1930).

(3) Lindner, *Monatsh.*, **28**, 1041 (1908).

(4) Bernoulli, Wege and Jakubowicz, *Helv. Chim. Acta*, **2**, 511 (1919); **4**, 1018 (1921).

(5) Jakubowicz, *Z. anorg. Chem.*, **121**, 113 (1922).

(6) Burk and Davis, *J. Phys. Chem.*, **35**, 146 (1931).

(7) Hinshelwood, *J. Chem. Soc.*, **17**, 156 (1920).

(8) Marshall, *Rec. trav. chim.*, **51**, 233 (1932).

change from a straight line to an upward curve showed the point at which decomposition began to take place. To check the result obtained in this way malonic acid was heated and a stream of air free from carbon dioxide was passed over the acid and then through a solution of barium hydroxide. The temperature at which a precipitate was first formed agreed within two degrees with the temperature found with the use of the expansion method.

In obtaining the results reported in this paper the two methods, improved and made more accurate, were applied to a number of compounds. The method based on expansion (called the physical method) was found to be more delicate than the one based on the detection of carbon dioxide (the chemical method). The former gave cracking temperatures from one to three degrees lower than the latter in the eleven cases in which the two methods were used. The detection of the first appearance of barium carbonate was rendered more certain by the use of a specially constructed nephelometer.

The following conclusions can be drawn from the results. (1) All the twelve monosubstitution products studied began to crack below the decomposition temperature of malonic acid (129°). The least effective group in lowering the cracking temperature was phenyl (123°) and the most effective *sec*-butyl (98°). The order of the primary alkyl group was as follows: methyl, isobutyl, ethyl, *n*-butyl, isoamyl, *n*-propyl, allyl.

(2) The introduction of a side chain in the α-position increased to some extent lability toward heat of the C–C bond: C_2H_5 110°, iso-C_3H_7 103°; C_3H_7 99°, *sec*-butyl 98°; $(CH_3)(C_2H_5)$ 123°, (CH_3) (iso-C_3H_7) 110°. Comparisons in β-and γ-positions are limited to single cases. In the β-position there was decreased lability—*n*-C_3H_7 99°, iso-C_4H_9 115°; in the γ-position increased lability—*n*-C_4H_9 108°, iso-C_5H_{11} 101°. A similar alternation in chemical reactivity of the hydrogen atom in alcohol has been shown to take place when side chains are introduced in these positions.[9]

(3) All the five di-substituted malonic acids containing one kind of radical which have been studied decompose at higher temperatures than the corresponding monosubstituted acids: $(CH_3)_2$ 150°, CH_3 120°, $(C_2H_5)_2$ 126°, C_2H_5 110°; (*n*-$C_3H_7)_2$ 143°, *n*-C_3H_7 99°; (iso-$C_3H_7)_2$ 182°, iso-C_3H_7 103°; (iso-$C_4H_9)_2$ 140°, iso-C_4H_9 115°.

(4) All the di-substituted acids containing two unlike radicals decompose below the temperature of malonic acid. The most striking effect of lack of symmetry on cracking temperatures is shown in the case of the (CH_3) (iso-C_3H_7) derivative (110°). The dimethyl derivative breaks at 150° and the di-isopropyl at 182°. These results and those summarized in paragraph 3 will be of service in interpreting the cracking of paraffin hydrocarbons containing straight and branched chains.

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[9] Norris and Cortese, THIS JOURNAL, 49, 2640 (1927).

(5) The order of the effect of the introduction of alkyl radicals into methylmalonic acid, as far as determined, is the same as that obtained when these same radicals are introduced into malonic acid, namely: CH_3, C_2H_5, n-C_4H_9, iso-C_3H_7, n-C_3H_7, $CH_3CH{=}CH_2$.

(6) The order of the effect of the introduction of C_2H_5, n-C_4H_9 and n-C_3H_7 into chloromalonic acid is the same as in paragraph 5.

(7) Only three compounds which contained a benzene ring have as yet been studied. In phenylmalonic acid (123°) the radical had less effect than methyl (120°) on the lability toward heat of the C–C bond. The introduction of a chlorine in the ortho position changed the cracking temperature from 123 to 102°. Benzyl (115°) had a slightly greater labilizing effect than CH_3 (120°).

Some preliminary observations were made of the influence of the presence of a variety of substances on the cracking temperature of malonic acid with the expectation of finding catalysts that lower the temperature at which the carbon to carbon bond breaks in this compound. It was shown that malonic acid could be held for at least three hours in a stream of air at 115–116° without the formation of carbon dioxide. Mixtures of the acid (0.5 g.) and the contact substance (0.25 g.) were held at this temperature for one-half hour or less and air free from carbon dioxide was drawn over the mixture and then through a solution of barium hydroxide. If any decomposition occurred, the time required to yield a precipitate of barium carbonate was noted. The most efficient substances and the time in minutes required to produce decomposition were as follows: water (3), acetic acid (3), $KHSO_4$ (5), Mg powder (8), Al powder (10), zinc chloride (10). When the acid was slowly heated in the presence of calcium oxide free from carbonate, carbon dioxide was formed at 90°.

The acids were prepared by using the methods described in the literature. The determination of the melting points in the usual way of most of these acids is not a test of purity because they decompose, in many cases, before they begin to melt. The neutralization equivalents were accurately determined.

Since the melting points obtained in capillary tubes are dependent on the rate of heating and the rate of decomposition of the acids, determinations of melting points on a Dennis[10] bar were made. The temperatures obtained were reproducible. When the melting point was below the cracking temperature, the two methods gave similar results. When the acids began to decompose before melting, the melting point in a capillary tube was below that found with the use of the bar. The greatest difference was shown by phenylmalonic acid (cracking temperature 122.8°). In the tube it melted at 139–140° with much decomposition, and on the bar at 169°.

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(10) Dennis and Shelton, THIS JOURNAL, 52, 3128–3132 (1930).

Experimental Details

Preparation of Malonic Acid Derivatives.—The alkyl substitution products were made by methods based on the work of Conrad.[11] The aryl derivatives were made by the method of Rising and Stieglitz.[12] Advantage was taken of the fact that monoalkylated malonic esters are saponified in two hours or less by a hot 50% aqueous solution of potassium hydroxide, whereas the disubstituted esters require concentrated alcoholic potash and ten or more hours of refluxing. It was possible therefore to separate largely a monoalkyl acid from a dialkyl derivative formed simultaneously. The ethyl esters formed in the syntheses were fractionated under diminished pressure before hydrolysis. The disubstituted esters were prepared from the purified monosubstituted esters. The acids were crystallized several times before use. The neutralization equivalent of the acids is the best criterion of purity that can be used. The melting points on the Dennis bar were determined on two occasions and the results obtained checked.

The results obtained with the acids prepared for this investigation are given in Table I.

TABLE I

PROPERTIES OF THE MALONIC ACID DERIVATIVES USED

(For Chloromalonic Acids, see Table II)

Radical	Neutralization equivalent			Melting point, °C.			Av. decomp. temp., phys. method, °C.
	Calcd.	Found		Cap. tube observed	Dennis bar	Literature	
None	52.01	51.99	52.18	129–131	134	130.5–135.6	129
iso-C_3H_7	73.04	73.07	73.02	87–91	88	87	103
$CH_2CH{=}CH_2$	72.03	71.74	72.08	97–101	95	102–105	99
sec-C_4H_9	80.05	80.30	80.44	75–76	76	76	98
iso-C_5H_{11}	87.05	86.86	86.99	95–96	96	93	101
C_6H_5	90.03	89.93	90.14	139–141	169	152–153	123
o-ClC_6H_4	107.28	107.2	107.4	128–130	133	139	101
$C_6H_5CH_2$	97.04	97.09	97.26	119–120	120	117–121	116
CH_3, CH_3	66.03	66.09	66.11	193–194	195	186–193	150
C_2H_5, C_2H_5	80.05	80.17	80.11	126–127	126	121–125	126
CH_3, C_2H_5	73.04	73.05	72.90	121–122	121	117.5–122	123
CH_3, *n*-C_3H_7	80.05	80.18	79.90	102–106	105	106–107	98
CH_3, iso-C_3H_7	80.05	79.86	79.54	120–124	126	124	110
CH_3, $CH_2CH{=}CH_2$	79.04	78.84	79.14	89–91	85	134	96
CH_3, *n*-C_4H_9	87.05	86.97	87.36	98–99	98	99–101	109
C_6H_5, C_2H_5	104.05	104.5	104.9	153–155	182	...	117

Determination of Decomposition Temperatures.—The so-called *physical method* was based on the same principle used in the earlier work but the apparatus was improved. The tube to contain the material was made of Pyrex glass tubing 14 cm. in length and 1 cm. in diameter. It was connected with a long horizontal capillary tube (internal diameter 2 mm.) enclosed in a larger glass tube carrying a meter stick which served to measure the position of a mercury bead as it moved when the temperature of the reaction tube was raised. In order to avoid the possible irregular adhesion of the bead to the tube the latter was furnished with a tapper (a door bell buzzer) which was set in motion thirty seconds before a reading was made. The decomposition tube was placed in a large tube containing Nujol and this into a short-necked liter flask containing the same liquid and surrounded by asbestos paper. A calibrated thermometer was placed in the inner bath. The horizontal capillary tube was first made level. This was accomplished by moving the tube to such a position that the mercury bead did not move when the tube was tapped at intervals of about 5 cm.

A volume of the acid to be investigated equivalent to about 0.5 g. of malonic acid

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(11) Conrad, *Ann.*, **204**, 127 (1880).

(12) Rising and Stieglitz, THIS JOURNAL, **40**, 723(1918).

was placed in the decomposition tube, which had been disconnected from the capillary tube. The tube was closed by a rubber stopper and the temperature of the bath raised rapidly to about 50° below the decomposition temperature, and thereafter at the rate of one degree in two minutes. At about 25° below the decomposition temperature the side arm of the reaction tube was connected with the capillary tube. After equilibrium was established the position of the bead was recorded for every two degrees rise in temperature. Before decomposition the position of the bead plotted against temperature gave a straight line. As soon as decomposition began a smooth upward curve was obtained. The inclination of this curve to the straight line varied with the different acids.

The position of the mercury bead, after pyrolysis began, was determined by the volume of the carbon dioxide and of the vapor of the organic acid produced. Since the latter varied with the acid used, the curves cannot be used to determine the relative rates of decomposition. The differences between the curves in certain cases were so great, however, that they indicated markedly different rates of decomposition. The number of divisions on the scale over which the bead moved as the acid was heated from its cracking temperature to 5° above this temperature was determined. A few of the results were as follows: $(C_6H_5)(C_2H_5)$ 26, $(CH_3)(C_2H_5)$ 24, $(C_6H_5)(CH_3)$ 20, malonic acid 12, iso-C_5H_{11} 5, $CH_3CH{=}CH_2$ 5, $(CH_3)(C_3H_7)$ 3. It is evident that the first three acids decomposed much more rapidly than the last three. There appears to be no direct relationship between the cracking temperatures, melting points and rates of decomposition.

In the *chemical method* of determining the cracking temperature the same apparatus and procedure were used, except that the capillary tube was replaced by a nephelometer and a stream of air was drawn through the entire length of the reaction tube and the nephelometer. The air before use was passed through three spiral wash bottles which contained a strong solution of sodium hydroxide, a trap, a similar wash bottle containing concentrated sulfuric acid, a train containing cotton wool to remove traces of spray and finally through a tube containing phosphorus pentoxide and glass wool. A small plug of cotton wool was placed between the decomposition tube and the nephelometer to prevent any of the solid acid from being carried along with the stream of air.

The nephelometer, which was contained in a closed box, was so arranged that observations were made of two half circles of reflected light which touched and each of which had passed through a tube containing a solution of barium hydroxide. When the solutions were placed in the tubes the presence of carbon dioxide was avoided. The temperature at which the tube connected with the rest of the apparatus first showed a cloudy appearance was taken as the cracking temperature. Before making a measurement air was drawn through the complete apparatus with the acid in place and the absence of carbon dioxide demonstrated. Before use the acids were crystallized from appropriate solvents and heated overnight in a vacuum oven at about 35°.

In Table II are given the results obtained by us and, for use in the comparison of the effect of the nature of the radicals on cracking temperatures, those of Norris and Young and of Marshall.

The purified chloromalonic acids were furnished us by Mr. E. B. Hershberg of this Laboratory. The melting points determined in the usual way were as follows: Cl, C_2H_5, 110.2°, Cl, n-C_3H_7 98.8–99.3; Cl, n-C_4H_9 90.7–91.8°.

It will be seen from Table II that the chemical method gave results slightly higher than the physical method. The latter responds more quickly to decomposition since the movement of the mercury bead is brought about by both the carbon dioxide and the vapor of the acid formed.

TABLE II

CRACKING TEMPERATURES OF MALONIC ACID DERIVATIVES

The letter after the temperatures recorded refers to the measurements of Norris and Young. The solvents listed are those used in this Laboratory.

Substituent	Solvent for recrystallization	Decomposition temperatures, °C. Physical method	Chemical method	Physical method by Marshall
None	Benzene	128 Y		
None	Acetone and toluene	128.8, 128.2	131	133.7
None	Water	117.4, 117.1	127	
CH_3	Benzene	120 Y		117
C_2H_5	Benzene	110 Y		112
n-C_3H_7	Benzene	99		102
iso-C_3H_7	Benzene	90 Y, 103.5, 102	104	108
$CH_2CH=CH_2$	Benzene	99, 98.6		
n-C_4H_9	Benzene	108 Y	109	
iso-C_4H_9				115
sec-C_4H_9	Carbon tetrachloride	99.6, 97.2	99.5	
iso-C_5H_{11}	Benzene and pet. ether	101.4, 101.0	103	
CH_3, CH_3	Acetone and toluene	149.4, 150		
CH_3, CH_3	Water	153, 153.5	155	171
CH_3, C_2H_5	Ether and pet. ether	122.6, 123.6		
C_2H_5, C_2H_5	Chloroform	125.8, 125.5		130
CH_3, *n*-C_3H_7	Benzene	97.8, 97.6		
CH_3, iso-C_3H_7	Benzene	109.6, 110	111	
CH_3, $CH_2CH=CH_2$	Ether and pet. ether	96.5, 95.8		
CH_3, *n*-C_4H_9	Benzene and pet. ether	109.3–108.5	111	
n-C_3H_7, *n*-C_3H_7				143
iso-C_3H_7, iso-C_3H_7				182
iso-C_4H_9, iso-C_4H_9				140
C_6H_5	Acetone and toluene	122.8	125	
o-ClC_6H_4	Benzene	101.2, 103.2	102	
$C_6H_5CH_2$	Benzene	116.4, 114.6	118	
$C_6H_5C_2H_5$	Furfural, benzene and pet. ether	116.8	119	
Cl, C_2H_5	Benzene	97.2, 95		
Cl, *n*-C_3H_7	Benzene	76.4, 75.7		
Cl, *n*-C_4H_9	Benzene	83.6, 82.8	87	

It is necessary, however, to remove the last traces of solvent from the acids before they are used. It is probable that the difference between the results obtained by the use of the two methods with malonic acid crystallized from water is due to the fact that all the solvent had not been removed.

It is possible that the presence of a trace of solvent may act catalytically and thus lower the cracking temperature. Notwithstanding these sources of error, which were guarded against, we believe the results obtained by the physical method are the more reliable. The relationship between the cracking temperatures of the acids is independent of the method used.

The difference between the results of Marshall and those of Norris and Young in the case of malonic acid (5.7°) and isopropyl malonic acid (18°) led to a re-study of these compounds. In the case of malonic acid by the physical method the average of the new determinations is 128.5°. Norris and Young reported 128° and Marshall obtained 133.7° with what was considered the best sample of his acid. A re-investigation of the sample of isopropylmalonic acid used in the earlier investigation (cracking temperature 90°) gave 92° by the physical and 104–105° by the chemical method. The acid apparently had not been freed from the solvent. A new sample of the acid gave by the physical method 103.5 and 102° and by the chemical method 104°. These results are in closer agreement with Marshall's determination—108°.

Difficulty was encountered in determining the cracking temperature of isopropylmalonic acid by the physical method. The acid melted about 15° below the temperature at which it decomposed. While the acid was melting the movement of the mercury bead either stopped or was greatly reduced. Before cracking began the normal movement set in. As a result of this behavior the plotted points before cracking did not lie on a continuous straight line but on two straight lines at the same inclination, connected by a horizontal or slightly inclined curve. The extent to which this phenomenon is noticeable is determined by the rapidity of heating between the melting and cracking points. Too rapid heating leads to an apparent cracking temperature that is too low. Similar behavior was shown by the allyl and the methyl-*n*-butyl compounds.

We have no explanation to offer for the difference between our result and that of Marshall in the case of dimethylmalonic acid. Marshall modified the method of Norris and Young by replacing mercury in the capillary tube by an organic liquid that wet the tube. This change does not appear to us to be advantageous and may be the reason why Marshall obtained figures in most cases slightly higher than ours.

Effect of the Presence of Certain Substances on the Cracking Temperature of Malonic Acid.—The method used has been outlined in the first part of this paper. Since the experiments were of a preliminary nature

TABLE III

EFFECT OF CONTACT SUBSTANCES ON THE DECOMPOSITION OF MALONIC ACID

The times noted are those required to produce carbon dioxide

Contact substance	Observation	Contact substance	Observation
None	No test in 3 hours	$ZnCl_2$	10 min.
Al powder	10 min.	CaO	Test at 90°
Sb powder	No test in $^1/_2$ hr.	Fe_2O_3	No test in $^1/_2$ hr.
Cu powder	No test in $^1/_2$ hr.	PtO	Slight test in 15 min.
Fe filings	No test in $^1/_2$ hr.	$KHSO_4$	5 min.
Zn dust	No test in $^1/_2$ hr.	H_2O (2 drops)	3 min.
Mg powder	8 min.	CH_3COOH (2 drops)	3 min.
Ni powder	Slight test 15 min.	None	Satd. soln. of acid test at 92°
S	Slight test in $^1/_2$ hr.		
I_2	No test in $^1/_2$ hr.	Satd. soln. of acid + $AlCl_3$ + HCl in H_2O	Test at 86°
$AlCl_3$	No test in $^3/_4$ hr.		

to find what substances should be carefully studied, ordinary c. p. materials were used without further purification. The oxides used were shown to yield no carbon dioxide when treated with an acid. All the substances were dried overnight in a vacuum oven at 30° and kept in a vacuum desiccator until used. About 0.5 g. of the acid and 0.25 g. of the substance were ground together and placed in the reaction tube. The chemical method was used. The temperature of the bath was 115–116°. The results are given in Table III.

Summary

1. The temperatures have been determined at which a number of substituted malonic acids first begin to show evidence of decomposition when they are heated so that the temperature is increased at the rate of two degrees per minute.

2. The relationship is discussed between the composition, structure and the number of radicals present and the cracking temperatures so determined.

3. The results are of value in showing the effect of structure on the lability toward heat of a carbon to carbon bond in these compounds.

4. It is shown that certain contact substances lower the temperature at which this bond is broken by heat.

Cambridge, Massachusetts

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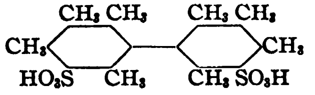
[Contribution from the Chemical Laboratory of the University of Illinois]

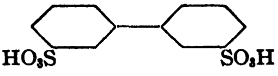
Stereochemistry of Diphenyls. XXXIV.[1] Preparation and Properties of 2,2′,4,4′,5,5′,6,6′-Octamethyldiphenyl-3,3′-disulfonic Acid and Diphenyl-3,3′-disulfonic Acid

By A. E. Knauf[2] and Roger Adams

The resolution of 2,2′,4,4,′5,5′,6,6′-octamethyldiphenyl-3,3′-disulfonic acid (I) into optical antipodes has been accomplished. The active forms could not be racemized by any of the usual methods. On the other hand, attempts to resolve the corresponding diphenyl 3,3′-disulfonic acid (II) have been unavailing.



I



II

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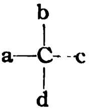
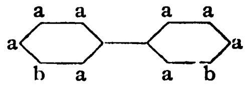
[1] For the previous paper in this field see VanArendonk, Becker and Adams, This Journal, 55, 4230 (1933). See also Adams and Yuan, *Chem. Rev.*, 12, 261 (1933).

[2] Submitted as a thesis for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

This pair of compounds illustrates more strikingly than do other recorded cases a peculiarity of the stereoisomerism in the diphenyl and related series, which has not hitherto been explicitly pointed out.

The theory of van't Hoff predicts that any compound of the type  $a{-}\overset{b}{\underset{d}{C}}{-}c$ should exist in two stereoisomeric forms—assuming that the substituents a, b, c, d are univalent radicals which are not in themselves optically active. It is of the very essence of this theory that the existence of the two isomers is in no wise dependent upon the specific properties of the individual radicals, but is conditioned solely by the fact that they are all four different from one another. Like considerations hold when van't Hoff's idea is applied to compounds containing more than one asymmetric carbon atom; they are equally applicable to cyclic and to open chain compounds; they account for the stereoisomerism in the allene and spiro series; and they apply also to molecular dissymmetry such as that observed among the inositols. Even the stereoisomerism attributed to elements other than carbon can be explained without change in this aspect of the van't Hoff theory. In all these cases, the number of stereoisomers depends upon the structure of the molecular skeleton, the number of univalent substituents of each particular kind, and the way in which the univalent substituents are distributed to satisfy the free valence of the skeleton. The specific properties of the univalent substituents themselves should be without effect on the number of isomeric forms.

But the stereoisomerism in the diphenyl and related series is not in accord with this widespread rule. The pair of substances cited above illustrates the impossibility of predicting the number of stereoisomeric forms of a compound defined only by the type formula III.



III

If (a) is the hydrogen atom there is one form; if (a) is the methyl radical there are two. In other words, the number of forms is not a type property of the molecule, but depends upon the specific nature of the univalent substituents.

It is thus evident that no mere extension of the van't Hoff theory (such as the one introduced by Werner) can account for the stereoisomerism in the diphenyl and other similar series. A new and independent assumption is indispensable. The various hypotheses hitherto suggested show that considerable freedom of choice in this field still exists. But to get along without some addition to the classical theory is formally impossible.[3]

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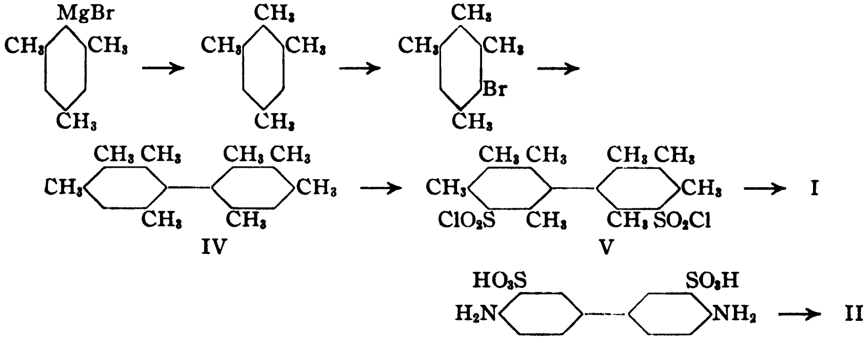
(3) The problem to obtain two compounds of the type described in this research was started over five years ago but owing to experimental difficulties, has just been completed. During this period Dr. J. K. Senior has continuously expressed his interest in this particular investigation. He was kind enough to present his views in writing and the authors have adopted them without essential change for the introductory paragraphs of this communication.

Experimental

Compounds I and II were prepared by the following series of reactions



During the course of the investigation the 3,3′-diaceto and 3,3′-dichloroaceto derivatives of 2,2′,4,4′,5,5′,6,6′-octamethyldiphenyl were prepared but could not be successfully used.

2,2′,4,4′,5,5′,6,6′-Octamethyldiphenyl (Diisoduryl) (IV).[4]—In a 3-liter three-necked flask fitted with a mechanical stirrer, reflux condenser and 500-cc. dropping funnel were placed 24.3 g. of magnesium turnings, 70 g. of bromoisodurene,[5] 100 cc. of anhydrous ether and a few crystals of iodine. By warming the flask without stirring the reaction was started and allowed to proceed for a few minutes. Mechanical stirring was started and a solution of 143 g. of bromoisodurene in 400 g. of dry ether was added at such a rate that the ether refluxed steadily. The addition of the halide required about three hours, after which stirring was continued and the mixture heated on a steam cone for about twelve hours. The flask was then cooled and when the contents were at 10°, 150 g. of finely powdered anhydrous cupric chloride was added as rapidly as the heat of the reaction permitted. To avoid loss of ether and to prevent hydration of the cupric chloride, the cupric chloride was placed in an Erlenmeyer flask which was connected by means of rubber tubing to the large end of an adapter. The small end of the adapter was attached to the flask containing the Grignard solution at the opening which previously held the dropping funnel. By properly inclining and shaking the Erlenmeyer flask the rate of flow of the powdered cupric chloride could be regulated. After addition of all of the solid, the ether was kept refluxing gently and vigorous stirring was continued for about twenty-four hours. At the end of this time the mixture was poured slowly into cracked ice and hydrochloric acid sufficient in amount to dissolve all of the solid (cuprous chloride). The ether layer was washed, and dried with anhydrous sodium sulfate. After removing the ether the remaining liquid was fractionally distilled under reduced pressure. The fraction boiling above 145° at 4 mm. was taken as crude diisoduryl. It solidified on cooling and was purified by crystallization from glacial acetic acid and washing the crystals with methyl alcohol; white crystals, m. p. 121–122°, yield 56 g. (21%).

Anal. Calcd. for $C_{20}H_{26}$: C, 90.15; H, 9.85. Found: C, 90.34; H, 10.07.

2,2′,4,4′,5,5′,6,6′-Octamethyldiphenyl-3,3′-disulfonyl Chloride (V).—Two grams of diisoduryl was added in small quantities with stirring to 10 g. of chlorosulfonic acid which

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(4) This substance was first made by W. M. Moyer as part of an earlier investigation.

(5) Isodurene was obtained by the procedure described by Smith and MacDougall, THIS JOURNAL, 51, 3003 (1929), and was brominated by the method used by these authors for making bromomesitylene from mesitylene.

had been previously cooled to 0° by a freezing mixture of ice and salt. The diisoduryl dissolved completely and after the mixture had stood for one hour it was poured onto ice. After washing, the solid was dried in a desiccator containing sulfuric acid. Purification from benzene gave white crystals, m. p. 159–160°, yield 2.8 g. (77%).

Anal. Calcd. for $C_{20}H_{24}O_4S_2Cl_2$: Cl, 15.33. Found: Cl, 15.50.

Preparation and Resolution of 2,2′,4,4′,5,5′,6,6′-Octamethyldiphenyl-3,3′-disulfonic Acid (Diisoduryl Disulfonic Acid).—A mixture of 2.3 g. of V and a solution of 1 g. of sodium hydroxide in 150 cc. of water was boiled until solution was complete (about eight hours). The excess of sodium hydroxide was neutralized with dilute hydrochloric acid and the solution filtered free of solid material. The solution of sodium diisoduryl disulfonate was heated to boiling and added slowly to a solution of 4.1 g. of strychnine hydrochloride in 200 cc. of water. After standing for about twelve hours, the white crystals which had formed were filtered off and after drying first in an oven at 120° for four hours and then in an Abderhalden drier at 100° and 4 mm. pressure weighed 2.3 g. Evaporation of the mother liquor to a volume of 100 cc., followed by standing for twelve hours, yielded another crop of crystals which, when dried by the above method, weighed 2.2 g. Both fractions melted at 252–255° (with dec.). Further evaporation gave no crystals and when dry a dark brown rather gummy residue was obtained.

Rotation. 0.1786 g. of first fraction made up to 10 cc. in 80% methyl alcohol at 20° gave α_D −0.25°; $l = 1$; $[\alpha]^{20}_D$ −14°.

Anal. Calcd. for $C_{62}H_{70}O_{10}N_4S_2$: N, 5.12. Found: N, 5.03.

The amount of salt recovered amounted to approximately 85% of the theoretical quantity and since recrystallization of each fraction from water gave products with the same rotation, it became obvious that water was not a satisfactory solvent for resolution.

Resolution of Distrychnine Diisoduryl Disulfonate.—The two fractions were combined and 3 g. of material was dissolved in 400 cc. of boiling absolute alcohol. On standing for twelve hours, the solution deposited a considerable quantity of white crystals, 0.9 g. Evaporation of the mother liquor to 200 cc. followed by standing for twelve hours gave a further crop of crystals, 0.5 g. These fractions, both of which had a melting point of 252–255° dec., were combined.

The mother liquor was evaporated to dryness and 1.5 g. of light brown salt obtained, m. p., 248–251° dec.

Rotation. (Less soluble salt) 0.2680 g. made up to 10 cc. in 80% methyl alcohol at 20° gave α_D −0.57; $l = 1$; $[\alpha]^{20}_D$ −21.3°.

Recrystallization from absolute alcohol did not alter the melting point.

Anal. Calcd. for $C_{62}H_{70}O_{10}N_4S_2$: S, 5.85. Found: S, 5.70.

Rotation. (Less soluble salt) 0.3140 g. made up to 10 cc. in 80% methyl alcohol at 20° gave α_D −0.68°; $l = 1$; $[\alpha]^{20}_D$ −21.6°.

Rotation. (More soluble salt) 0.2905 g. made up to 10 cc. with 80% methyl alcohol at 20° gave α_D −0.30; $l = 1$; $[\alpha]^{20}_D$ −10.3°.

This fraction was not recrystallized.

Anal. Calcd. for $C_{62}H_{70}O_{10}N_4S_2$: S, 5.85. Found: S, 5.74.

1-Ammonium Diisoduryl Disulfonate.—A suspension of 0.6580 g. of less soluble strychnine salt in 15 cc. of dilute aqueous ammonia (1:15) was extracted four times with 10-cc. portions of chloroform and the rotation of the resulting aqueous solution determined.

Rotation. The volume of the tube used was 9.2 cc. and this contained theoretically 0.1697 g. of ammonium diisoduryl disulfonate, α_D −0.21; $l = 1$; $[\alpha]^{20}_D$ −11.4°.

Continued extractions with chloroform did not change the rotation.

Evaporation of 9.2 cc. of solution to dryness gave 0.1701 g. of salt (theoretical quantity 0.1697 g.). After drying in an Abderhalden dryer at 140° it was analyzed.

Anal. (Parr bomb) Calcd. for $C_{20}H_{32}O_6N_2S_2$: S, 13.91. Found: S, 13.74.

d-**Ammonium Diisoduryl Disulfonate.**—This was prepared in a similar manner to the *l*-salt from 0.6668 g. of the more soluble strychnine salt.

Rotation. The volume of the tube used was 9.2 cc. and this contained theoretically 0.1720 g. of ammonium salt: α_D +0.21°; $l = 1$; $[\alpha]^{20}_D$ +11.2°.

Additional extractions did not change the rotation.

Evaporation of 9.2 cc. of this solution to dryness gave 0.1725 g. of ammonium salt (theoretical quantity 0.1720 g.).

Anal. Calcd. for $C_{20}H_{32}O_6N_2S_2$: S, 13.91. Found: S, 13.69.

Racemization Experiments.—Continued boiling of the ammonium salts of both *l* and *d* forms gave no change in rotation.

2,2′,4,4′,5,5′,6,6′-Octamethyl-3,3′-dichloroacetodiphenyl (Dichloroacetyldiisoduryl).—A mixture of 100 cc. of carbon disulfide, 2.6 g. of diisoduryl, and 7 g. of chloroacetyl chloride was cooled in a freezing mixture of ice and salt and 6 g. of anhydrous aluminum chloride was gradually added. After the mixture had been mechanically stirred for one hour, the carbon disulfide was removed by distillation and the aluminum chloride decomposed by adding ice and concentrated hydrochloric acid. The solid material which separated was filtered off and recrystallized from glacial acetic acid as white needles, m. p. 183–184°, yield 3.1 g. (74%).

Anal. Calcd. for $C_{24}H_{28}O_2Cl_2$: Cl, 16.93. Found: Cl, 16.95.

Attempts to replace the chlorines by dialkylamino groups or an amino gave ill-defined products. Attempts to oxidize to —COCOOH or —COOH groups were also unsuccessful.

2,2′,4,4′,5,5′,6,6′-Octamethyl-3,3′-diacetodiphenyl (Diacetyldiisoduryl).—A solution of 2.5 g. of diisoduryl and 2.5 cc. of acetyl chloride in 40 cc. of carbon disulfide was cooled in an ice-bath and 5 g. of anhydrous aluminum chloride was gradually added. After the mixture had stood for two hours, the carbon disulfide was removed by evaporation and the aluminum chloride decomposed by addition of ice and concentrated hydrochloric acid, m. p. 184°, yield, 2.8 g. (84%).

Anal. Calcd. for $C_{24}H_{30}O_2$: C, 82.28; H, 8.57. Found: C, 82.40; H, 8.82.

Attempts to oxidize the $COCH_3$'s to —COCHO by the method of Riley with selenium dioxide resulted in failure.

Diphenyl-3,3′-disulfonic Acid.—This acid was prepared from benzidine disulfonic acid[6] by a modification of the method of G. Schultz and W. Kohlhaus.[7] Sulfuric acid was used for the diazotization instead of hydrochloric acid. The potassium and barium salts of the diphenyl disulfonic acid were prepared for use in making the alkaloidal salts.

(*a*) **Brucine Salt.**—A solution of 11.8 g. of brucine in 61.5 cc. of 0.49 *N* hydrochloric acid and 40 cc. of water was prepared by boiling. This was added to a hot solution of 6.39 g. of dried potassium diphenyl disulfonate in 50 cc. of water. On cooling, a quantity of brucine salt crystallized which when dried at 110° weighed 15.5 g. (94% of the theoretical), m. p. 268–270° with softening at 244°.

Rotation. (Salt dried *in vacuo* at 110°) 0.3235 g. made up to 10 cc. in pyridine gave $\alpha_D = -0.82°$; $l = 1$; $[\alpha]^{29}_D$ −25.3°.

Recrystallization or fractionation from water or alcohol always gave products of identical rotation and melting point.

Anal. Calcd. for $C_{58}H_{62}O_{14}N_4S_2$: S, 5.81. Found: S, 5.71.

(*b*) **Strychnine Salt.**—This salt was made in a similar way to the brucine from 6.68 g. of strychnine in 20 cc. of *N* sulfuric acid and 200 cc. of water and 5.86 g. of dried

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(6) Griess and Dinsberg, *Ber.*, **22**, 2464 (1889).

(7) Schultz and Kohlhaus, *ibid.*, **39**, 3342 (1906).

barium diphenyl disulfonate in 100 cc. of water. On filtration and evaporation to dryness the salt was obtained.

It was purified from methyl alcohol and norite. All fractions gave the same rotation.

Rotation. (Dried *in vacuo* at 110°) 0.2363 g. made up to 10 cc. with pyridine gave α_D -0.71; $l = 1$; $[\alpha]^{\circ}_{D}$ $-30°$. Essentially the same rotation was observed at room temperature.

Anal. Calcd. for $C_{54}H_{64}O_{10}N_4S_2$: S, 6.52. Found: S, 6.41.

Attempts were also made to obtain the morphine, cinchonine, cinchonidine and quinine salts but in each case only oils were obtained.

Summary

Diisoduryl disulfonic acid has been resolved. Diphenyl 3,3′-disulfonic acid could not be resolved. These two compounds represent a pair which illustrate strikingly that the stereoisomerism in the diphenyl series cannot be defined by type formulas.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

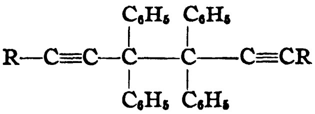
Rearrangements of Polyines. VI. Tetra-biphenyl-di-tertiary-butylethinylethane

BY JUNE CHIEN-YU TSAO AND C. S. MARVEL

It has been shown that hexa-substituted ethanes containing acetylenic groups on the central ethane carbon atoms readily undergo rearrangement to give more stable hydrocarbons.[1] The ease with which this rearrangement occurs appears to be dependent on the strength of the carbon–carbon single bond in the central ethane linkage.

$[R—C\equiv C]_3—CC—[C\equiv C—R]_3$

A



$$R—C\equiv C—\underset{C_6H_5}{\overset{C_6H_5}{C}}—\underset{C_6H_5}{\overset{C_6H_5}{C}}—C\equiv CR$$

B

None of the hexa-alkylethinylethanes (type A) undergo this rearrangement except under the influence of heat.[2] On the other hand all of the tetra-aryl dialkylethinylethanes (type B) which have been investigated[3] have changed to isomeric hydrocarbons at room temperature or below.

A remarkable increase in the degree of dissociation of hexaarylethanes[4] and of tetraaryldialkylethanes[5] has been observed when a biphenyl group has been introduced in place of a phenyl group in these molecules. This

[1] See THIS JOURNAL, 55, 3712 (1933), for the previous paper in this field.

[2] (a) Salzberg and Marvel, *ibid.*, 50, 1737 (1928); (b) Ozanne and Marvel, *ibid.*, 52, 5267 (1930); (c) Davis and Marvel, *ibid.*, 53, 3840 (1931).

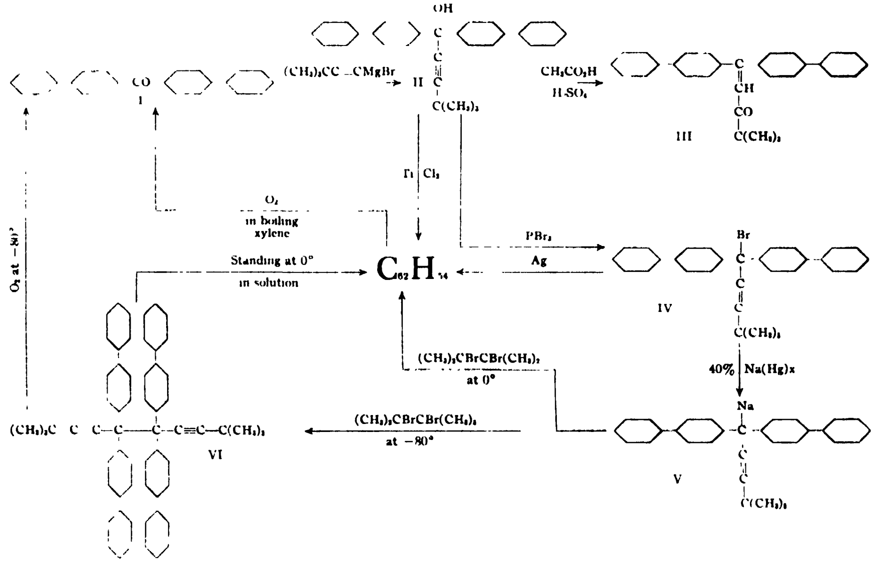
[3] (a) Stampfli and Marvel, *ibid.*, 53, 4057 (1931); (b) Munro and Marvel, *ibid.*, 54, 4445 (1932); (c) Harmon and Marvel, *ibid.*, 55, 1716 (1933).

[4] Schlenk, Weickel and Herzenstein, *Ann.*, 372, 1 (1910); *Ber.*, 43, 1753 (1910).

[5] Conant and Schultz, THIS JOURNAL, 55, 2098 (1933).

fact has suggested that the synthesis of tetrabiphenyl-di-*tert*-butylethinylethane (VI) would make it possible to test in a critical way the idea that the weakness of the central ethane linkage is the principal causative factor in this type of polyine rearrangement.

The reactions involved in the present study are as follows



Most of the reactions were carried out by methods which have been discussed in earlier papers of this series. It is of great interest to note that no evidence for the existence of tetradiphenyl-di-*tert*-butylethinylethane (VI) could be obtained until the reaction between the sodium derivative (V) and tetramethylethylene bromide was carried out at about −80°. The desired hydrocarbon was not isolated, for even at this low temperature the rearrangement to the more stable isomeric hydrocarbon $C_{62}H_{54}$ (VII) took place rapidly. Evidence which supports our view that the desired ethane was present in the cold solution was obtained by oxidation experiments. When the ethane was prepared at about −80°, a solution which absorbed oxygen with great avidity was obtained. After oxidation was complete, the only product which could be isolated from this solution was di-biphenyl ketone (I).

The rearranged hydrocarbon $C_{62}H_{54}$ was not only obtained when solutions of the true ethane were allowed to stand until rearrangement had occurred but was also produced by the reduction of the carbinol (II) by titanium trichloride and by the action of silver on the bromide (IV). These last reactions have previously been shown to give rearrangement products from the corresponding phenyl substituted derivatives.[6] A

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(6) (a) Salzberg and Marvel, THIS JOURNAL, 50, 2840 (1928); (b) Sweet and Marvel, *ibid.*, 54, 1184 (1932).

solution of the rearranged hydrocarbon, $C_{62}H_{54}$, did not absorb oxygen at room temperature. When its solution in boiling xylene was treated with oxygen, oxidation did occur and di-biphenyl ketone was obtained in slightly less than 50% yields. This is further evidence that in this type of rearrangement at least half of the molecule retains its original structure.[3c]

The similarity of the properties of tetra-biphenyl-di-*tert*-butylethinylethane with those of tetra-biphenyl-di-*tert*-butylethane is of interest. Conant and Schultz[5] have found that this latter hydrocarbon is dissociated in benzene solution at 5° to the extent of nearly 75%, is extremely sensitive to oxygen, and its solutions are colored even at −78°. Oxidation of both compounds by oxygen gives di-biphenyl ketone. The compound with the two acetylenic groups seems to be more sensitive to oxygen, since it oxidized very rapidly at about −80°.

Experimental

Dibiphenyl-*tert*-butylethinylcarbinol.—This carbinol was prepared from 110 cc. of 1.875 *N* ethylmagnesium bromide solution, 20 g. of *tert*-butylacetylene and 60 g. of dibiphenyl ketone according to the usual procedure for such reactions.[2a] The dibiphenyl ketone was so insoluble in ether that it was necessary to add it in an ether suspension rather than in solution. The ketone was added in 20-g. portions suspended in 500 cc. of ether and the addition required about two days. The reaction mixture was filtered to recover about 30 g. of unreacted ketone and the ether solution was then worked up in the usual fashion. The crude carbinol obtained by evaporating the ether solution weighed 40 g. and melted at 170–171°. It was recrystallized three times from petroleum ether (b. p. 65–110°) and then melted at 172–173° in a capillary tube and at 180–181° on a Maquenne block. The yield of purified product was 36 g. (85% of the theoretical amount based on the unrecovered ketone).

Anal. Calcd. for $C_{31}H_{28}O$: C, 89.35; H, 6.80. Found: C, 89.85, 89.95; H, 6.85, 6.9.

Rearrangement of the Carbinol.—The carbinol underwent the Meyer and Schuster rearrangement[7] when treated with sulfuric acid in acetic acid. Two grams of carbinol in 10 cc. of glacial acetic acid was treated with 1 cc. of concentrated sulfuric acid and 1.5 g. of the unsaturated ketone (III) melting at 142° was obtained. Recrystallization of the unsaturated ketone from petroleum ether (b. p. 65–110°) raised the melting point to 144–145°.

Anal. Calcd. for $C_{31}H_{28}O$: C, 89.35; H, 6.8. Found: C, 89.18; H, 7.06.

Di-biphenyl-*tert*-butylethinylbromomethane.—Treatment of 6 g. of the carbinol in 100 cc. of dry ether with 2 g. of phosphorus tribromide at 0° for about six hours in the usual fashion[2a] gave 4 g. of crude bromide. Recrystallization of this product four times from a mixture of absolute alcohol and absolute ether gave 1.5 g. of product which melted at 135–136°.

Anal. Calcd. for $C_{31}H_{27}Br$: Br, 16.67; mol. wt., 479. Found: Br, 16.79, 16.89; mol. wt. (Rast), 538.

The bromide was sensitive toward moisture and on standing in the air changed to the yellow unsaturated ketone which was formed by the rearrangement of the carbinol by the action of acids.

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(7) Meyer and Schuster, *Ber.*, **55**, 819 (1922).

Action of Silver on the Bromide.—The ether solution of the bromide prepared from 6 g. of carbinol and 2 g. of phosphorus tribromide was shaken with 5 g. of molecular silver for about sixty hours. The solution was filtered and the solvent removed. The residue was recrystallized four times from absolute alcohol and absolute ether. The yield was 2 g. of a product which softened at 130° and decomposed at 135–148° in a capillary tube. On the Maquenne block the compound melted at 166°.

Anal. Calcd. for $C_{62}H_{54}$: C, 93.18; H, 6.82; mol. wt., 798. Found: C, 92.38, 92.69; H, 6.87, 7.00; mol. wt. (cryoscopic in benzene), 711, 799.

This hydrocarbon was stable in the air for short periods and could be kept for months in a vacuum desiccator. On long standing in the air, it turned yellow.

Action of Titanium Trichloride on the Carbinol.—A solution of 4 g. of the carbinol in 10 cc. of alcohol was heated with 20 cc. of 20% solution of titanium trichloride for about two hours.[6b] From the reaction mixture 3 g. of product melting at 128–140° was obtained. After recrystallization from absolute alcohol and ether, 1.8 g. of the hydrocarbon $C_{62}H_{54}$, m. p. 166° (Maquenne block), was obtained.

Di-biphenyl-*tert*-butylethinylmethyl-sodium.—The ether solution of the bromide prepared from 6 g. of the carbinol was shaken with 16 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen for about twenty-four hours. The solution became warm within five minutes and was deep red in color within an hour. The alkyl was not isolated but was used in solution. Pure bromide was used in some experiments and toluene and petroleum ether were also used as solvents. Several attempts were made to convert the sodium alkyl to the corresponding acid and carbomethoxy derivative by treatment with dry carbon dioxide and methyl chlorocarbonate, respectively. No crystalline products were obtained.

Tetra-biphenyl-di-*tert*-butylethinylethane.—In a nitrogen atmosphere a toluene solution of the above sodium derivative prepared from 1 g. of the bromide was cooled to about −80° by means of carbon dioxide snow and acetone. To the cold solution was added dropwise about 10 cc. of a 20% solution of tetramethylethylene bromide in ether. The red color of the sodium alkyl disappeared in about thirty minutes.

This solution was connected with a gas buret containing oxygen and the absorption of the gas was noted. The reaction mixture was shaken by hand to facilitate absorption. Within thirty minutes 187.7 cc. of oxygen was taken up and no more was absorbed when the mixture was allowed to stand at about −80° or after warming the mixture to room temperature.

The toluene solution was a yellow-orange in color and was acidic to moist litmus. No acid could be separated in sufficient quantity for identification by extracting with alkalies and reacidifying the aqueous extract. The toluene solution was evaporated and the residue treated with absolute alcohol. The solid thus obtained was washed with ether to remove the excess tetramethylethylene bromide. The residue (0.05 g.) after this treatment was found to be di-biphenyl ketone; m. p. 230–234°. When mixed with an authentic specimen of the ketone, this product did not depress the melting point.

The same experiment was repeated using 2 g. of bromide. After the addition of the tetramethylethylene bromide, the solution was divided into two equal portions. One portion was treated with oxygen as above and 158.5 cc. of oxygen was absorbed in twenty-six minutes. By allowing the reaction mixture to warm up to room temperature, a further 129.2 cc. of oxygen was absorbed. From the toluene solution a small amount of di-biphenyl ketone (0.049 g.) was isolated as before.

The other portion of the solution obtained in the above experiment was allowed to come to room temperature and to stand for about ten hours. After that time the solution would no longer absorb oxygen. On evaporating the solvent and recrystallizing the residue, about 0.5 g. of the hydrocarbon $C_{62}H_{54}$ was obtained. This product was not pure but recrystallization gave 0.1 g. of pure hydrocarbon, m. p. 166° (Maquenne block).

The reaction between di-biphenyl-*tert*-butylethinylmethyl-sodium and tetramethylethylene bromide was also carried out at room temperature and at 0°. The solutions thus obtained did not absorb oxygen and the only product which could be isolated from them was the rearranged hydrocarbon, $C_{62}H_{54}$.

Some Reactions of the Rearranged Hydrocarbon, $C_{62}H_{54}$.—A solution of 0.1 g. of the hydrocarbon $C_{62}H_{54}$ in 2 cc. of dry carbon tetrachloride did not decolorize two drops of a 5% solution of bromine in carbon tetrachloride.

Treatment of 1 g. of the hydrocarbon with 8 cc. of 40% sodium amalgam under nitrogen in ether solution produced a purple-red colored alkali metal derivative. No acid was isolated when this was treated with carbon dioxide. The color of this metal derivative was somewhat different from that of the sodium compound prepared from di-biphenyl-*tert*-butylethinylbromomethane.

The hydrocarbon $C_{62}H_{54}$ dissolved in petroleum ether would not absorb oxygen at room temperature. When a solution of 0.8 g. of the hydrocarbon in 100 cc. of boiling xylene was maintained in contact with oxygen for seven days, a total of 164 cc. of oxygen was absorbed. After the third day crystals began to separate. Toward the end of the period the solution became dark yellow in color. When no more oxygen was absorbed the solution was filtered and evaporated. From the residue 0.5 g. of the original hydrocarbon was recovered. The crystals which had separated from the xylene weighed 0.2 g. and melted at 230–234°. They were identified as di-biphenyl ketone. The yield of the ketone was about 50% based on the hydrocarbon which was used up in the reaction.

Summary

1. Tetra-biphenyl-di-*tert*-butylethinylethane has been prepared in solution. It is rapidly oxidized by oxygen at about −80° to yield di-biphenyl ketone. At 0° it rapidly rearranges to a stable isomer $C_{62}H_{54}$. The ease with which this change occurs is further evidence that weakness of the ethane linkage is the chief causative factor in this rearrangement.

2. The hydrocarbon $C_{62}H_{54}$ has also been obtained by the action of silver on di-biphenyl-*tert*-butylethinylbromomethane and by the reduction of di-biphenyl-*tert*-butylethinylcarbinol with titanium trichloride. This hydrocarbon in boiling xylene is slowly oxidized by oxygen to give about a 50% yield of di-biphenyl ketone.

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Studies of Polymerization and Ring Formation. XVIII. Polyesters from ω-Hydroxydecanoic Acid

BY WALLACE H. CAROTHERS AND FRANK J. VAN NATTA

The obvious importance of simple synthetic models as an aid in studying macromolecular materials has been emphasized repeatedly by Staudinger,[1] who has used polystyrene, polyoxymethylene, polyacrylic acid, etc., for this purpose. Our own researches on condensation polymers were started with the idea that the fact of a proposed model's being synthetic is of little value unless the method of synthesis is rational, *i. e.*, unless it is sufficiently clear-cut to leave no doubt concerning the structure of the product. Polystyrene may, for example, serve as a simplified model of rubber, but it has the disadvantage that the method used in its synthesis (a spontaneous polymerization of unknown mechanism) furnishes no certain clue to its structure. The independent demonstration of its structure presents the same difficulties as does rubber; in fact today the formula of rubber can be written with more assurance than that of polystyrene.

In the first paper of this series[2] it was pointed out that bifunctional condensations frequently proceed by known mechanisms. In the second paper[3] it was shown for polyesters derived jointly from dibasic acids and glycols that the reaction consists exclusively in esterification while the average size of the product molecule increases progressively with the completeness of the reaction. Rational, deliberate control over the average molecular weight is thus made possible, and, as was shown later,[4] by using more drastic conditions molecules of average weight greater than 20,000 can be obtained. Meanwhile a study of the self-esterification of ω-hydroxydecanoic acid was presented by Lycan and Adams,[5] who concluded that the products must be formulated like the polyesters referred to above.

We have now greatly extended the range of polyesters derived from ω-hydroxydecanoic acid and have obtained the series of fractions of different average molecular weights shown in Table I. The structure of these polyesters $HO[—(CH_2)_9CO—O—]_n(CH_2)_9CO—OH$ follows from the method used in their synthesis (see Experimental Part) and the fact that they can be hydrolyzed quantitatively to ω-hydroxydecanoic acid. The only important uncertainty is the distribution, in a given sample, of the molecular weight about the observed average (*i. e.*, the degree of homogeneity). However, since these esters are all crystalline solids and since the mer or unit of the chain is quite long, the homogeneity is probably better than in the case of such materials as polystyrene which can be purified only by fractional precipitation or extraction. Moreover, a determination of the molecular weight of the highest member of the series by the Svedberg ultracentrifugal method indicates that the weight of most of the molecules lies fairly close to the observed average. It is indeed our opinion that this series of polyesters is more definitely and certainly established in identity and structure than any similar series of macromolecular compounds yet described.

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[1] Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

[2] Carothers, THIS JOURNAL, 51, 2548 (1929).

[3] Carothers and Arvin, *ibid.*, 51, 2560 (1929).

[4] Carothers and Hill, *ibid.*, 54, 1559 (1932).

[5] Lycan and Adams, *ibid.*, 51, 625, 3450 (1929).

TABLE I

POLYESTERS FROM ω-HYDROXYDECANOIC ACID

Mol. wt.	M. p., °C.	d^{25}_4	n^{85}_D	Spinnability	Tensile strength
780	66–67	1.0957	1 4494	Absent	
1720	72–74	1.0935	1.4506	Absent	
3190	74–75	1.0877	1.4517	Absent	
4170	74–76	1.0814	1.4517	Absent	
5670	73–75	1.0751	1.4518	Very short fibers. No cold drawing	
7330	74–75	1.0715	1.4517	Long fibers, but cold drawing absent	Very weak
9330	75–76	1.0668	1.4518	Long fibers which cold draw	Very weak
16900	77–78	1.0627	....	Easily spins and cold draws	13.1 Kg./mm.^{2}
20700	77–78	1.0632	....	Spins with difficulty but easily cold draws	12.3 Kg./mm.^{2}
25200	75–80	1.0621	1.4515	Spins above 210° and cold draws	7 0 Kg./mm.^{2}

TABLE II

MOLECULAR WEIGHTS OF POLYESTERS

Observed mol. wts. (by titration)			Average	Observed mol. wts. (by other methods)	Calculated length of molecule in Å.
776	784		780	930 (in boiling benzene)	60
1707	1722		1720	1620 (in boiling benzene)	123
3188	3201		3190	Not measured	188
4114	4226		4170	Not measured	313
5626	5717		5670	Not measured	440
7327	7329		7330	Not measured	570
9331	9335		9330	Not measured	730
16890	17110	16790	16900	Not measured	1320
20380	20930		20700	Not measured	1610
24240	25760	25660	25200	26700 (ultracentrifuge)	1970

Molecular Weights.—Molecular weights were estimated by titration with standard alcoholic potash of the polyesters dissolved in a chloroform–alcohol mixture. Phenolphthalein was used as an indicator. This method applied to pure lauric acid gave values agreeing sharply with the theoretical (200.4, 199.6 and 199.2 as against 200.2). Observed values for the polyesters are shown in Table II. It is interesting to note that no difficulty was encountered in titrating the highest member of the series where the acid hydrogen is only one part in 25,000.

The average equivalent weight measured by titration will of course be identical with the average molecular weight only if each molecule bears a terminal carboxyl in the manner required by the indicated structure.

The accidental loss of terminal carboxyls under the conditions of preparation used seems rather improbable, but indication of the absence of such loss is provided by independent estimations of molecular weight. The boiling point method furnished values for the first two members agreeing, within the probable experimental error, with the much more sharply reproducible values determined by titration. For compounds above molecular weight 3000, in our experience, boiling-point or freezing-point methods are not self-consistent within 10%, and above 10,000 they are practically worthless. We were, however, very fortunate in being able to obtain a value for the highest polymer by the Svedberg ultracentrifugal method.[6] The agreement is all that could be desired.

Physical Properties.—The polyesters below 10,000 dissolve rapidly and completely in cold chloroform or benzene and in hot acetone, ethyl acetate and acetic acid. They are practically insoluble in hot alcohol, ligroin or water. The highest members show diminished solubility in benzene and in hot acetone and ethyl acetate. They dissolve copiously in chloroform, but solution occurs only slowly and is preceded by some swelling. At *ca.* 110° the first member of the series is a highly viscous liquid while the highest member is a transparent resin that is too stiff to flow and sufficiently elastic to offer resistance to permanent deformation.

Lycan and Adams have pointed out[5] that the melting point of self-esters of hydroxydecanoic acid increases with increasing molecular weight up to 1000, but changes little between 1000 and 9000. As the data of Table I show, there is also no further increase between 9000 and 25,000. The polyesters separate from solution in the form of white powders which give sharp x-ray powder diffraction patterns. At least in the lower members of the series crystallinity can also be demonstrated by microscopic observation. A very dilute solution of the 3190 ester in butyl acetate, when examined at a magnification of 400, showed the separation of tiny flat glittering plates. The molten esters in thin layers crystallize very rapidly, but with the lower members one can observe the crystallization to start with the emergence and growth of innumerable doubly refracting centers, apparently spherulites. At a magnification of 900 the growth appears to involve the intermeshing of radiating clusters of needles.

The masses resulting from crystallization of the molten polyesters are opaque solids. The lower members are waxy and brittle; when fractured they show no planes of cleavage. The highest members are harder and so horny and tough that they can scarcely be fractured.

In Table I are listed the densities of the solid esters at 25°. The values *diminish* as the molecular weight rises, quite rapidly at first and then more slowly until at a molecular weight of 16,900 they become almost constant.

[6] Kraemer and Lansing, THIS JOURNAL, 55, 4319 (1933).

This at first sight is very surprising. Polymerization usually involves an increase in density. There is, for example, an increase of 23% in passing from chloroprene to polychloroprene.[7] The interpretation of the present case can scarcely be attempted in the absence of data on the molten esters, which are not yet available; but it is easy to imagine that the longer the molecules are the more difficulty they will have in lining themselves up perfectly in the crystal lattice. The refractive indices of the molten esters at 85° are presented in Table I. There is a slight increase from 780 to 1720, a smaller increase from 1720 to 3190, and beyond that no further change.

Fiber Formation.—In a previous paper[8] it was shown that linear polyesters of molecular weight above 10,000, when melted or dissolved, can be spun into fibers. The initial filaments are opaque and fragile, but when stress is applied to them they are readily elongated several fold and then remain *permanently extended*. The stretching is accompanied by a loss of opacity, and an enormous increase in tensile strength and pliability. Examination by x-rays shows the presence of fiber orientation. These fibers are, we believe, the first examples of a synthetic material being obtained in the form of fibers having any considerable degree of strength, orientation and pliability. The analogies in chemical structure with cellulose and silk are especially interesting, and the esters of the present paper provide some data (Table I) on the relation between molecular weight and fiber-forming ability. Until a molecular weight of 5670 is reached, the viscosity and coherence of the molten esters are so low that they do not yield continuous filaments. The ester of molecular weight 7330 furnished continuous filaments which, however, could not be stretched and oriented. The 9330 ester could be stretched, but the oriented fibers were too weak to permit the determination of tensile strength. Oriented fibers from the 16,900 ester had a tensile strength of 13.1 kg./sq. mm. or 1.36 g. per denier, which is in the same range as good regenerated cellulose fibers. The value for the 20,700 ester (12.3 kg./sq. mm.) differs from that for the 16,900 ester by an amount that probably lies within the experimental error. The tensile strength of the 15,200 ester is, however, definitely much lower. It is exceedingly improbable that the fiber strength of completely oriented molecules rises to a maximum and then falls off as the length of the molecule increases. On the other hand, the degree of orientation that can be produced by cold-drawing probably depends upon other factors besides molecular weight. An unusually high temperature (210°) was required to soften the 25,200 ester sufficiently to permit spinning, and its relatively low tensile strength may therefore reasonably be ascribed to factors associated with orientation. It may be observed that the ability to form strong, highly oriented fibers does not appear until the molecular length reaches some value lying between 700 and 1300 Å.

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(7) Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).

(8) Carothers and Hill, *ibid.*, **54**, 1579 (1932).

Viscosity and Other Properties.—The viscosities of dilute solutions of these polymers in tetrachloroethane have been carefully measured. The results already reported and discussed[9] show that Staudinger's simple empirical equations relating viscosity to molecular weight[1] are satisfied fairly well until the molecular weight reaches 16,900; beyond this point the viscosities rise more rapidly than the equations require. Staudinger has assumed that the relations between viscosity and molecular weight established for compounds below 10,000 will hold for compounds of higher molecular weight. The data referred to above provide the first experimental test of this assumption, and for the polyesters under consideration it is shown to be not strictly valid. Molecular weights that have been assigned to cellulose, rubber, high polystyrenes, etc., on the basis of viscosity measurements must therefore be considered as subject to considerable uncertainty.

Study of the physical properties of polyesters derived from hydroxydecanoic acid is being continued, and further results will be reported in future papers.

Experimental Part

Preparation of Polyesters.—The lowest members of the series were obtained by heating ω-hydroxydecanoic acid at 150° in an ordinary distilling flask provided with a receiver. Diminished pressure and higher temperatures were used for higher members of the series; the highest members (above 10,000) were obtained by heating the hydroxydecanoic acid or its lower polyesters in a molecular still consisting essentially of a suction flask into which a water-cooled test-tube was inserted to act as a condenser. The products were crystallized several times to increase their homogeneity. Typical procedures are indicated below.

Polyester of Molecular Weight 4170.—Twenty grams of the acid was heated at 150–175° under atmospheric pressure for one and one-half hours, then at 200° at 1 mm. pressure for eight hours. The resulting waxy product was crystallized by dissolving in a small amount of boiling chloroform and adding several volumes of hot acetone. The product had an apparent equivalent weight of 3906. A second crystallization from hot acetone by slow cooling raised the equivalent weight to 4170. The ester was obtained as a chalky powder, soluble in chloroform and benzene and in hot acetone, ethyl acetate and acetic acid. Hot alcohol, ligroin or water did not dissolve it appreciably.

Anal. Calcd. for $HO{-}[(CH_2)_9{-}CO{-}O]_{24}{-}H$: C, 70.22; H, 10.66; mol. wt. 4101; saponification equivalent, 170.8. Found: C, 70.35, 70.70; H, 10.69, 10.88; mol. wt. by titration, 4114, 4226; saponification equivalent, 170.7.

Polyester of Molecular Weight 9330.—Thirty-six grams of the acid was heated for seven hours at 120–175° at 1 mm. pressure, then for twenty-five hours at 225° at 1 mm. It was crystallized several times from hot acetone by slow cooling and was obtained as a pure white powder. It did not differ appreciably from polymer 4170 in solubility.

Anal. Calcd. for $HO{-}[(CH_2)_9{-}CO{-}O]_{55}{-}H$: C, 70.39; H, 10.66; mol. wt. 9376; saponification equivalent 170.5; Found: C, 70.56; H, 10.87; mol. wt. by titration: 9335, 9331; saponification equivalent 169.6.

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(9) Kraemer and Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).

Polyester of Molecular Weight 20,700.—Fifteen grams of hydroxydecanoic acid was heated at 230° in a molecular still for thirty hours. During the first few hours a considerable amount of distillate (dimer and unchanged acid) collected on the condenser. This was removed and the residue in the flask was stirred frequently. At the end of the reaction the mass was plastic when hot. It was purified by dissolving in a small amount of hot chloroform, then adding several volumes of acetone and allowing the product to crystallize by cooling. This polymer was less soluble than lower members in benzene or in hot acetone or ethyl acetate. Solution was slow and was preceded by some swelling.

Anal. Calcd. for $\mathrm{HO{-}[(CH_2)_9{-}CO{-}O]_{121}{-}H}$: C, 70.47; H, 10.66; mol. wt. 20,605; saponification equivalent 170.3. Found: C, 70.72, 70.29; H, 10.62, 10.47; mol. wt. by titration, 20,380, 20,930; saponification equivalent 170.8.

Saponification of the polyesters by alcoholic alkali always resulted in complete solution, indicating the absence of any appreciable amount of non-ester ingredient, and the following experiment showed that the product of saponification was the initial hydroxydecanoic acid: 0.3097 g. of the 13,600 polyester was saponified with alcoholic sodium hydroxide; the alcohol was removed and the solution was acidified and extracted with ether. Evaporation of the ether yielded 0.34 g. (99.3% of the theoretical amount) of hydroxydecanoic acid.

During the preparation of the polyesters a small amount of the cyclic dimeric lactone, a 22-membered ring $\overline{\mathrm{O{-}(CH_2)_9{-}CO{-}O{-}(CH_2)_9{-}C}}\mathrm{O}$, was always formed. It was obtained in the form of needles from dilute alcohol; m. p. 95–96°.

Anal. Calcd. for $\mathrm{C_{20}H_{36}O_4}$: C, 70.58; H, 10.67. Found: C, 70.07, 70.04; H, 10.53, 10.55.

This lactone has already been prepared by Lycan and Adams[5] indirectly from the potassium salt of hydroxydecanoic acid and acetic anhydride followed by dry distillation at 400–500°.

Summary

A series of polyesters prepared from ω-hydroxydecanoic acid and ranging in molecular weight from 780 to 25,200 is described. Strong, oriented fibers are obtained only from members having molecular weights above 9330. The influence of molecular weight on some other physical properties is discussed.

WILMINGTON, DEL.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, McGILL UNIVERSITY]

Studies on Lignin. X. The Identity and Structure of Spruce Lignins Prepared by Different Methods

BY FRITZ BRAUNS AND HAROLD HIBBERT

The numerous investigations relating to the structure of lignin have been carried out on products prepared by a variety of different processes involving the use of extraction media of widely varying chemical characteristics. These media can be divided into two classes: (I) those capable of functioning as solvents for the lignin and (II) reagents capable of dissolving the cellulose. Class I can be divided into two groups Ia and Ib.

To Class Ia belong such solvents as alcohols,[1] polyalcohols, chlorohydrins[2] and phenols[3] used in conjunction with a catalyst such as hydrochloric acid; while Class Ib includes caustic alkalies.[4] Class II comprises solvents such as solutions of cuprammonium hydroxide,[5] strong mineral acids (HCl and H_2SO_4)[6,7] and trichloroacetic acid.[8]

The question as to the identity of the lignin, isolated by these various methods, with the "native lignin," as present in the original wood, still remains a matter of great uncertainty. Furthermore, no evidence has been adduced, as yet, to show that the lignins isolated by the various methods bear any direct relationship to one another.

The reason for this is to be found in the very reactive nature of the lignin complex and its tendency to undergo marked alteration in structure under the influence of chemical reagents.

Previous investigations have indicated that the use of alcohols and polyalcohols gives a lignin which has apparently undergone little or no structural change during the process of isolation.[2] It therefore seemed of interest to investigate more fully the properties and structure of "methyl alcohol lignin" and to compare this with "glycol lignin" on the one hand and, on the other hand, with lignin isolated by the use of (a) concentrated mineral acid, for instance hydrochloric ("Willstätter lignin")[6] and (b) a solution of cuprammonium hydroxide ("Freudenberg lignin").[5]

In a previous preliminary communication[9] it was found possible, on the basis of the analytical data obtained from an intensive study of carefully purified "glycol lignin" and "methyl alcohol lignin" to establish with reasonable certainty the empircal formula for "native lignin" as

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(1) E. Hägglund, *Cellulosechemie*, **8**, 69 (1927); **9**, 49 (1928).

(2) H. Hibbert and co-workers, *Can. J. Research*, **2**, 357, 364 (1930).

(3) R. O. Herzog and A. Hillmer, *Cellulosechemie*, **6**, 169 (1925).

(4) C. Dorée and L. Hall, *J. Soc. Chem. Ind.*, **43**, 257 (1924).

(5) K. Freudenberg, *Ber.*, **62**, 1814 (1929).

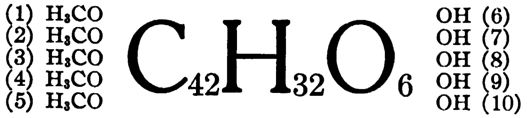
(6) R. Willstätter, *ibid.*, **46**, 2403 (1913); **55**, 2637 (1922).

(7) P. Klason, *Cellulosechemie*, **4**, 81 (1923).

(8) H. Hibbert, unpublished results.

(9) F. Brauns and H. Hibbert, *Pulp and Paper Mag. Can.*, **34**, 187 (1933).

$(C_{47}H_{52}O_{16})_x$ or $[C_{42}H_{32}O_6(OH)_5(OCH_3)_5]_x$. The smallest "building unit" is, accordingly



$$\begin{matrix}(1)\ H_3CO\\(2)\ H_3CO\\(3)\ H_3CO\\(4)\ H_3CO\\(5)\ H_3CO\end{matrix}\ C_{42}H_{32}O_6\ \begin{matrix}OH\ (6)\\OH\ (7)\\OH\ (8)\\OH\ (9)\\OH\ (10)\end{matrix}$$

with a molecular weight of 872.

The essential feature of this is the experimental establishment for *the first time* of a definite "building-unit" molecular weight representing the smallest unit possible which satisfies the analytical data corresponding with the introduction of *one* methoxyl group by the use of diazomethane.

It seemed probable that a connecting link between these two types of lignin might be established by their conversion into phenol condensation products, the analysis and properties of which should yield valuable information along structural lines.

This conclusion was based on the marked solubility shown by "glycol" and "methyl alcohol lignin," on the one hand, as compared with the insoluble character of "Willstätter" and "Freudenberg lignin" on the other, and the fact that both types give well-characterized, homogeneous soluble phenol condensation products in remarkably high yield.

Using this as a guiding principle it has been possible to prove definitely the structural identity of the lignin isolated by the use of the markedly different reagents grouped under Class I and Class II above.

Discussion of Results

Structural Identity of "Glycol" and "Methyl Alcohol Lignins."—In Table I are given the methoxyl values of various derivatives prepared from these two types of lignin. The methoxyl content of "glycol lignin," after treatment with diazomethane, is seen to increase from 16.8 to 21.0% and, on complete methylation, to 31.6%. The completely acetylated "glycol lignin" contains 14.1% OCH_3, or a ratio of (OCH_3) to (CH_3CO) of 1:1; in other words, for each methoxyl group there is one acetyl group present. Furthermore, acetylation of "glycol lignin" premethylated with

TABLE I

METHOXYL CONTENT OF GLYCOL AND METHYL ALCOHOL LIGNIN AND OF THEIR DERIVATIVES

Compound	Glycol lignin	MeOH lignin
Extraction medium	Glycol + HCl	MeOH + HCl
A, original lignin	16.85	21.2
B, fully acetylated product	14.1	17.9
C, original lignin (A) methylated with diazomethane.	21.0	24.9
D, acetyl derivative of (C)	17.5	21.7
E, fully methylated lignin prepared from (D)	31.6	32.4
Ratio of methoxyl to acetyl in (B)	1:1	6:4
Ratio of methoxyl to acetyl in (D)	6:4	7:3

diazomethane (product C) gives a product (D) containing 17.5% OCH_3 and containing a ratio of methoxyl to acetyl of 6:4.

"Methyl alcohol lignin," on methylation with diazomethane, shows an increase in methoxyl value from 21.2 to 24.9%, while on complete methylation the value obtained is 32.4%.

The fully acetylated "methyl alcohol lignin" has a methoxyl value of 17.9%, the ratio of (OCH_3) to CH_3CO being 6:4. The acetylation of "methyl alcohol lignin" premethylated with diazomethane (C) gives a product (D) containing methoxyl and acetyl in the ratio 7:3.

It follows from these analytical data, in particular from the ratios shown, that the smallest "native lignin" building unit must contain a total of ten hydroxyl groups five of which are methylated.

From the combustion analyses of the fully methylated derivatives (E), Table I, from their methoxyl contents, and from the ratio of methoxyl to acetyl present, it is possible to calculate their empirical formulas, which, as shown in Table II, are $C_{54}H_{66}O_{17}$ and $C_{52}H_{62}O_{16}$ for fully methylated "glycol" and "methyl alcohol lignin," respectively.

TABLE II

ANALYSES AND FORMULAS OF FULLY METHYLATED GLYCOL AND METHYL ALCOHOL LIGNIN

Compound, fully methylated	Glycol lignin	MeOH lignin
Carbon, %	65.65	66.2
Hydrogen, %	6.74	6.6
Methoxyl, %	31.6	32.4
Calcd. formula	$C_{54}H_{66}O_{17}$	$C_{52}H_{62}O_{16}$
Extended formulas:		
Fully methylated lignin derivs.	$C_{44}H_{36}O_7(OCH_3)_{10}$	$C_{42}H_{32}O_6(OCH_3)_{10}$
Original lignin derivs.	$C_{44}H_{36}O_7(OH)_5(OCH_3)_5$	$C_{42}H_{32}O_6(OH)_4(OCH_3)_6$

Since there are ten methoxyl groups in each fully methylated product their formulas are represented by $C_{44}H_{36}O_7(OCH_3)_{10}$ and $C_{42}H_{32}O_6(OCH_3)_{10}$, respectively.

It also follows that on complete methylation of the "glycol lignin" *five* methoxyl groups are introduced as compared with *four* in the case of the "methyl alcohol lignin." Deducting the new methoxyl groups from the respective formulas for the fully methylated compounds, there are obtained for "glycol lignin" and "methyl alcohol lignin" the formulas $C_{44}H_{36}O_7(OH)_5(OCH_3)_5$ and $C_{42}H_{32}O_6(OH)_4(OCH_3)_6$, respectively.

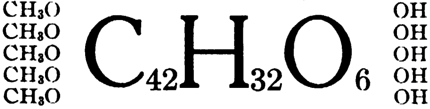
It is apparent that the former differs from the latter with respect to the (OCH_3), (OH) and the remaining radicals ($C_{44}H_{36}O_7$ and $C_{42}H_{32}O_6$), respectively.

Expanding the two formulas further to give $C_{42}H_{32}O_6(OH)_4(OCH_3)_5$-$OCH_2CH_2OH$ and $C_{42}H_{32}O_6(OH)_4(OCH_3)_5OCH_3$ it is evident that in the "methyl alcohol lignin" the glycol radical has been replaced by a methoxyl group. In other words, on extracting spruce wood meal with glycol, the hydrogen in one of the hydroxyl groups in the lignin is replaced by the glycol radical (C_2H_4O), while in "methyl alcohol lignin" the same hydrogen has been replaced by a methyl group.

Of the five free hydroxyl groups present in the "native lignin," one is characterized by its acidic property in that it undergoes methylation with diazomethane, and the methylated product so obtained is insoluble in sodium hydroxide solution.

The formula of the native lignin is readily deducible from that of the "glycol" and "methyl alcohol lignin" in that it is only necessary to deduct the number of C and H atoms present in the radicals C_2H_4O and CH_2 from the respective formulas. In both cases the same structural formula is obtained, *viz.*

$C_{42}H_{32}O_6(OH)_5(OCH_3)_5$



$$\begin{array}{c}CH_3O\\CH_3O\\CH_3O\\CH_3O\\CH_3O\end{array} C_{42}H_{32}O_6 \begin{array}{c}OH\\OH\\OH\\OH\\OH\end{array}$$

in which, as stated above, one hydroxyl group is known to possess an acidic, probably phenolic or enolic character, while a second hydroxyl group is characterized by ease of reaction with alcohols and hydrochloric acid.

Corresponding with this formula the methoxyl content of "native lignin" should be 17.5%, which agrees very well with the value calculated from the methoxyl content of the wood meal and its percentage of lignin and is also in agreement with the methoxyl content of Willstätter and Freudenberg lignin, the latter prepared by a preliminary mild hydrolysis with 1% sulfuric acid followed by extraction with cuprammonium hydroxide solution. The methoxyl content of "Willstätter lignin" varies from 14.2 to 15.8% depending on the mode of preparation. Assuming that it loses one methoxyl group due to the action of the strong hydrochloric acid during the course of preparation, this would lead to a structural formula $C_{42}H_{32}O_6(OH)_6(OCH_3)_4$ containing four methoxyl groups and a methoxyl content of 14.2%. As shown later, however, a "Willstätter lignin" if prepared at a low temperature and under mild conditions[10] has a higher methoxyl value (16.5% instead of that usually found (14.6%)). This surprising variation is due to contamination of the true Willstätter lignin with a by-product amounting, in general, to about 4–10%, left as an insoluble methoxyl-free residue in the conversion of both "Willstätter" and "Freudenberg" lignin into their phenol condensation products, so that the true methoxyl value is 17.5%.

On complete methylation the Freudenberg and Willstätter lignins are converted into products having a methoxyl content in each case of 32.2%, while the value calculated on the basis of the formula for fully methylated "native lignin" is 32.9% (Table II, $C_{42}H_{32}O_6(OCH_3)_{10}$). In other words;

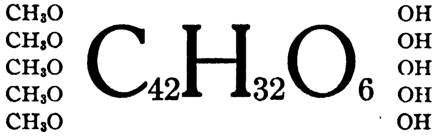
(10) L. Kalb and Lieser, *Ber.*, **61**, 1021 (1928).

hydroxyl groups are neither formed, nor removed, in the isolation of lignin by the alcohol extraction, or by the Willstätter or by the Freudenberg process.

If the formula suggested above for "native lignin" (Table III) is correct, it should be possible to deduce from it the structure of other types of lignin, *e. g.*, "phenol lignin."

TABLE III

Glycol lignin
$C_{42}H_{32}O_6(OH)_4(OCH_3)_5OCH_2CH_2OH$
Methyl alcohol lignin
$C_{42}H_{32}O_6(OH)_4(OCH_3)_5OCH_3$



$$\begin{matrix} CH_3O \\ CH_3O \\ CH_3O \\ CH_3O \\ CH_3O \end{matrix} C_{42}H_{32}O_6 \begin{matrix} OH \\ OH \\ OH \\ OH \\ OH \end{matrix}$$

Native lignin

Relation of "Phenol Lignin" to "Native Lignin."—Several papers dealing with the properties of phenol lignin have been published recently[3] but it seemed advisable to repeat and extend the work. In an investigation carried out by a co-worker, Miss Koerber, it was found that the phenol lignin obtained by extracting spruce wood meal with phenol (using hydrochloric acid as catalyst) could be separated into two approximately equal fractions (a) an ether-insoluble (OCH_3, 10.1%) and (b) ether-soluble (OCH_3, 5.4%).

In Table IV the analytical data relating to the former product (a) and its derivatives are shown. It can be seen that methylation with diazomethane yields a methylated product (C) with a methoxyl content of 21.6% from which, on further and complete methylation with dimethyl sulfate and sodium hydroxide, a fully methylated "phenol lignin" (E) (OCH_3, 28.2%) is obtained.

TABLE IV

METHOXYL CONTENT OF PHENOL LIGNIN AND DERIVATIVES PREPARED FROM SPRUCE WOOD MEAL, WILLSTÄTTER AND FREUDENBERG LIGNIN

	Spruce meal			
Phenol lignin made from.....	Ether-insol.	Ether-sol.	Willstätter	Freudenberg
A, original compound.......	10.1	5.3	12.3	12.0
B, acetylated................	7.8	..	9.6	..
C, meth. with diazomethane..	21.6	21.5	23.8	..
D, acetylated (C)...........	19.0	..	21.0	..
E, fully methylated..........	28.2	..	28.0	..
Ratio of methoxyl to acetyl in: B.....	1:2	..	5:7	..
Ratio of methoxyl to acetyl in: D.....	3:1	..	5:1	..

Acetylation of the ether-insoluble phenol lignin gives an acetyl compound (B) in which the ratio of methoxyl to acetyl groups is 1:2. The ether-insoluble phenol lignin, premethylated with diazomethane, yields on acetylation an acetyl derivative D having a ratio of methoxyl to acetyl of 3:1. This change in the ratio from 1:2 to 3:1, following methylation with diazomethane, indicates the presence of some new "free phenol hydroxyl groups" in the ether-insoluble phenol lignin.

The high yield of "phenol lignin" obtained (about 140%) shows that a large amount of phenol must have reacted with the lignin. It seems probable that *one* molecule of the phenol reacts in the same manner as glycol or methyl alcohol, giving rise, presumably, to formation of a phenol-ether. Apparently the remaining phenol molecules, reacting with the lignin, enter the lignin molecule in such a way that the phenolic hydroxyl groups remain free and the question thus arises as to the number of phenol groups so introduced.

The actual number entering into nuclear condensation with the lignin molecule was determined experimentally in the following way. "Glycol lignin," "glycol lignin" methylated with diazomethane, as well as the fully methylated "glycol lignin" were condensed separately with phenol and hydrochloric acid under the same usual operating conditions. The products thus obtained were then subjected to (a) methylation with diazomethane (b) complete methylation and (c) acylation. The methoxyl content of these products together with the ratio found for methoxyl to benzoyl shows that three new phenolic hydroxyl groups have been introduced into the respective phenol-glycol-lignin condensation products.

Three phenol molecules have evidently undergone nuclear condensation with the lignin molecule, whereby their respective hydroxyl groups remain uncombined, so that it was then possible to prepare from them well-characterized derivatives, homogeneous in character and remarkably light in color.

The analyses of the latter are also given in Table V, and, on the basis of the data shown, it is possible to calculate the formula for the original "phenol lignin," obtained directly from spruce meal (Table V).

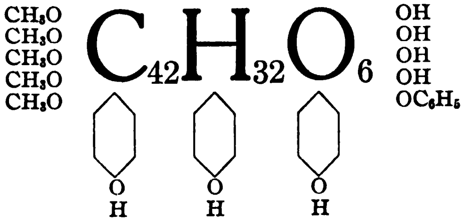
TABLE V

METHOXYL CONTENT OF THE PHENOL GLYCOL LIGNIN CONDENSATION PRODUCTS AND THEIR BENZOATES

Phenol deriv. of	Orig. prod.	Benzoyl deriv.	Ratio of methoxyl to benzoyl
Glycol lignin	13.1 (12.95)[a]	7.52 (7.6)	5:8
Glycol lignin meth. with diazomethane	16.1 (15.4)	9.52 (9.58)	6:7
Fully meth. glycol lignin	24.5 (24.45)		

[a] The figures in parentheses are the values calculated on the basis of the formula.

Phenol lignin



$$\begin{matrix} CH_3O \\ CH_3O \\ CH_3O \\ CH_3O \\ CH_3O \end{matrix} C_{42}H_{32}O_6 \begin{matrix} OH \\ OH \\ OH \\ OH \\ OC_6H_5 \end{matrix}$$

The theoretical methoxyl content of phenol lignin, as calculated from the formula given, is 12.6% whereas that actually found in ether-insoluble phenol lignin is only 10.1% and in the ether-soluble fraction 5.3%. If it is assumed, however, that in the preparation of phenol lignin from spruce wood meal, *one* methoxyl group is split off, a product would be obtained having the theoretical methoxyl value 10.1% and, as a matter of fact, all of the analytical values found for the various derivatives prepared from the ether-insoluble phenol lignin are then in agreement with the above formula (see Table IV).

The ether-soluble phenol lignin (CH_3O, 5.4%) apparently has the same fundamental building unit, since, on methylation with diazomethane, it yields the same product as the ether-insoluble (Table IVC). It differs from the ether-insoluble lignin in its methoxyl content only, in that it contains two instead of four methoxyl groups.

Application to Other Types of Lignin.—If it be correct that one type of lignin only is present in spruce wood, then the "Willstätter" as well as the "Freudenberg" spruce lignin should each possess the same building unit. On conversion of either into the characteristic ether-insoluble phenol condensation products, they should give in both cases an identical product corresponding with that prepared from glycol lignin with the single difference that the glycol radical has been replaced by a phenoxy group. This conclusion is based on the assumption that no side changes occur during the condensation reaction.

It was found experimentally that Willstätter lignin (OCH_3, 15.3%) gives, in quantitative yield, a phenol lignin with a methoxyl content of 12.3% (calculated 12.6%), leaving an undissolved residue amounting to from 8 to 10%. This insoluble residue is practically free from methoxyl and represents the impurity in the Willstätter lignin referred to above. The methoxyl content (12.3%) of the phenol lignin made from Willstätter lignin indicates that the true value of the methoxyl content of pure Willstätter lignin must be about 17.5%, that is, a value identical with the theoretical value as calculated from the methoxyl content of spruce wood meal taking into account the percentage of lignin present (see Table IV).

These facts find further confirmation in the analysis of the fully methylated products prepared (a) from ether-insoluble phenol lignin obtained directly from spruce meal and (b) from Willstätter phenol lignin, respectively, indicating the same methoxyl content (28.2 and 28.0%, respectively, Table IVE).[11]

Summary

1. Lignin has been isolated from spruce meal by the following methods: (a) action of glycol and hydrochloric acid; (b) use of methyl alcohol and hydrochloric acid; (c) extraction with phenol and hydrochloric acid; (d) Willstätter method; (e) Freudenberg method. The lignin isolated in each case was subjected to careful purification.

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[11] The authors desire to reserve the right of applying the technique described above to other types of lignin.

2. Well-characterized derivatives of each of these types of lignin have been prepared by methylation and acylation, respectively.

3. Each lignin type yields a well-characterized lignin–phenol condensation product, the analysis of which shows that they are derived from a common lignin building-unit.

4. This building-unit, representing the *native lignin* present in spruce wood, has the empirical formula $C_{47}H_{52}O_{16}$ or $C_{42}H_{32}O_6(OH)_5(OCH_3)_5$. Of the five free hydroxyl groups at least three are aliphatic in character, while one of the remainder is of an acidic type, either phenolic or enolic. The fifth hydroxyl group differs markedly from the remaining four and is characterized by its reactivity toward alkylating reagents such as hydrochloric acid and alcohols, phenols, etc.

5. The phenol condensation products from Willstätter and Freudenberg lignin are shown to possess the structure $C_{42}H_{35}O_6(OH)_4(OCH_3)_5(OC_6H_5)(C_6H_4OH)_3$.

MONTREAL, CANADA

RECEIVED SEPTEMBER 14, 1933
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Note

Benzyl Levulinate

BY PETER P. T. SAH, HSING HAN LEI AND HSI MENG FANG

In continuation of the studies of alkyl levulinates,[1,2] the benzyl ester has now been prepared. Of several methods tried, the following gave the best results. A mixture of 52 g. of levulinic acid, 160 g. of benzyl alcohol and 440 g. of toluene was treated with a current of dry hydrogen chloride until 7 g. was absorbed. The solution was boiled under reflux for twenty-four hours, whereupon the toluene was removed by distillation from an oil-bath at 125° and the residue fractionated under reduced pressure. A yield of about 65 g. of pure benzyl levulinate, b. p. 181–183° (17 mm.) was thus obtained. Sapon. eq. calcd. for $C_{12}H_{14}O_3$: 272.2; found 270.7. d_4^{20} 1.0935; d_4^{25} 1.0895; n_D^{20} 1.5090; n_D^{25} 1.5070.

The ester was characterized by a variety of hydrazones,[3] obtained in

Hydrazone		M. p., °C.		Analyses, % Found	Calcd.
Phenyl-	Rhombic plates	91–92	N	9.46	9.73
p-Tolyl-	Rectangular plates	99–100	N	9.03	9.17
p-Chlorophenyl-	Rectangular tablets	106–107	Cl	10.73	11.26
p-Bromophenyl-	Rectangular plates	103	Br	21.31	21.40

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(1) Sah and Ma, THIS JOURNAL, **52**, 4880 (1930); **54**, 3271 (1932).

(2) Schuette and Cowley, *ibid.*, **53**, 3485 (1931); Cowley and Schuette, *ibid.*, **55**, 387 (1933).

(3) Sah and Lei, *Sci. Rep. Nat. Tsinghua Univ. A*, **2**, 1, 7 (1933).

good yields as colorless crystals, possessing sharp melting points after recrystallization from light petroleum.

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RECEIVED JUNE 24, 1933
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COMMUNICATIONS TO THE EDITOR

CARROT LEAF CAROTENE

Sir:

We have isolated carotene from carrot leaves to determine whether it contains the components of carrot root carotene, or whether, like the majority of leaf carotenes reported, it is optically inactive. Only two optically active leaf carotenes, tea[1] and horse chestnut,[2] have been reported. The method of extraction described by Smith[3] was followed with minor modifications. We obtained 0.370 g. of recrystallized carotene from 6 kg. of leaf powder.

Specific optical rotations and melting points were determined on two samples, one recrystallized from petroleum ether–ethanol, the other from *n*-heptane.

Sample	M. p., °C. (Berl block, corr.)	$[\alpha]^{22}_{6678}$
Pet. ether–ethanol	175.7	+33.6° (36.6 mg. in 15 cc. benzene)
n-Heptane	176.8	+37.3° (33.0 mg. in 15 cc. benzene)

The specific rotation indicates approximately 10% of α-carotene.

The absorption spectrum in 95% ethanol was observed visually. Absorption maxima were found at 4533 Å. and approximately 4780 Å., nearly the positions of the maxima of β-carotene.

Adsorption on a column of Norit A (Pfanstiehl) from dichloromethane solution (method developed and shortly to be described by H. H. Strain) gave excellent resolution of the components. The first few drops of colored percolate, transferred to 95% ethanol, gave very sharp bands, with maxima at 4470 and 4738 Å., confirming the presence of α-carotene.

Adsorption on fibrous alumina from benzene and low boiling petroleum ether (50% by volume) showed the presence of a colored ring in the position to be expected for γ-carotene.[4] This ring was extracted and re-adsorbed from fresh solvent on a new column. When re-extracted, the solution was too dilute for satisfactory spectroscopic identification. How-

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(1) I. P. C. R. (Tokyo), **19**, 127 (1932).

(2) *Ber.*, **64**, 1349 (1931).

(3) J. H. C. Smith, *J. Biol. Chem.*, **96**, 35 (1932).

(4) *Ber.*, **66**, 407 (1933).

ever, the behavior of the ring is an indication of the presence of the γ-component.

It is concluded that carrot leaf carotene resembles carrot root carotene in its composition rather than the optically inactive carotenes hitherto found in most leaves.

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RECEIVED SEPTEMBER 29, 1933 PUBLISHED NOVEMBER 7, 1933

THE EFFECT OF THE SOLVENT ON THE POTENTIAL OF THE CHLORANIL ELECTRODE

Sir:

Since the original study of the chloranil electrode by Conant and Fieser,[1] it has been generally assumed both at Harvard and elsewhere[2] that "the potential of the saturated chloranil electrode against the hydrogen electrode is independent of the solvent (and has the value +0.664 volt at 25°")[3]

This assumption is, of course, well founded provided the solution studied is really in equilibrium with the unsolvated solid chloranil and its hydroquinone. Since this electrode has been chiefly used in glacial acetic acid, the following observations seem important.

In the course of certain measurements in this solvent (to be published later) it appeared that if the value +0.664 volt was accepted for the chloranil electrode, all the potentials measured differed from those obtained in the same system when a hydrogen electrode was used. The discrepancy disappeared if the value +0.680 volt was assigned to the chloranil electrode. We therefore measured directly the effect of the solvent on the potential of cells without liquid junction and containing a hydrogen and a chloranil electrode, with the result that Conant and Fieser's value of +0.664 volt was confirmed in 50% aqueous alcohol, while in glacial acetic acid and in 50% aqueous dioxane the values +0.680 volt and +0.715 volt were obtained.

These differences are due to the fact—previously overlooked—that tetrachlorohydroquinone is solvated in certain solvents, as has indeed long been known.[4] The solid phase in equilibrium with the saturated solution in glacial acetic acid is principally $C_6Cl_4(OH)_2 \cdot 2AcOH$, while in contact with dioxane solutions the solid phase is $C_6Cl_4(OH)_2 \cdot C_4H_8O_2$. From the observed differences of potential the free energies of solvation

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(1) Conant, Small and Taylor, THIS JOURNAL, **47**, 1959 (1925); Hall and Conant, *ibid.*, **49**, 3047 (1927); Conant and Chow, *ibid.*, **55**, 3745 (1933).

(2) Hall, *ibid.*, **52**, 5115 (1930).

(3) Conant and Chow, *loc. cit.*, p. 3748.

(4) See, *e. g.*, König, *J. prakt. Chem.*, [2] **70**, 33 (1904).

may be readily calculated and are found to agree well with the physical properties of the solvates.

It is clear that the potential of the chloranil electrode may be assumed independent of the solvent only if the electrode materials remain unsolvated under the conditions of the experiment.

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BERNARD O. HESTON
NORRIS F. HALL

RECEIVED OCTOBER 18, 1933 PUBLISHED NOVEMBER 7, 1933

THE VISCOSITY OF H^2H^2O

Sir:

The great difference between the conductivity of potassium chloride in H^2H^2O and in H^1H^1O which was found by Lewis and Doody [THIS JOURNAL, **55**, 3504 (1933)], made it desirable to ascertain the viscosity of heavy water. The time required to fill a pipet through a fine capillary, with a known head of pressure, was measured with a stop watch, the apparatus being enclosed in a constant temperature bath. At each temperature the heavy water was compared directly with ordinary pure water. The very close approximation to linearity between viscosity and isotopic composition is shown by the results obtained with water containing 70 and 90% of H^2. If η_1 and η_2 represent the viscosities of H^1H^1O and H^2H^2O, η_2/η_1 at 20° was found to be 1.249 by extrapolation from 90% and 1.244 by extrapolation from 70%.

The 90% sample was next compared with ordinary water between 5 and 35°. The results extrapolated to pure H^2H^2O show η_2/η_1 to be nearly linear with the temperature. The values interpolated at even temperatures are given in Table I, in which the first row gives the values of η_2/η_1 the second reproduces the values of η_1 given in "International Critical Tables," and the third the viscosity (in millipoises) of pure H^2H^2O obtained by multiplying the numbers in the first row by those in the second. We believe the results to be accurate within 0.5%.

VISCOSITY OF PURE H^2H^2O

t, °C.	5	10	15	20	25	30	35
η_2/η_1	1.309	1.286	1.267	1.249	1.232	1.215	1.198
η_1	15.19	13.10	11.45	10.09	8.95	8.00	7.21
η_2	19.88	16.85	14.51	12.60	11.03	9.72	8.64

These measurements of the viscosity, together with the measurement of the dielectric constant of H^2H^2O (accompanying communication), will permit the application of the Onsager equation to the conductivity measurements of Lewis and Doody. Since our experimental measurements of the viscosity were made, values of the viscosity of heavy water, at 20°, have been given by Selwood and Frost [THIS JOURNAL, 55, 4335 (1933)], but for some reason that we cannot understand, their results do not agree at all with our own.

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GILBERT N. LEWIS
RONALD T. MACDONALD

RECEIVED OCTOBER 23, 1933 PUBLISHED NOVEMBER 7, 1933

THE DIELECTRIC CONSTANT OF H^2H^2O

Sir:

By balancing capacities in an oscillating radio circuit, we have made a preliminary study of the dielectric constant of water in which the isotope H^2 constituted over 99% of the total hydrogen. A small cell (0.4 cc.) with parallel platinum plates was tested with various liquids and the capacity was found to be very nearly linear with the dielectric constant. The heavy water was then compared with ordinary conductivity water, at frequencies corresponding to 25, 34 and 40 meters. In the first experiments, the heavy water which had been distilled from sodium hydroxide in a vacuum was found to have a high conductivity ($\kappa = 3 \times 10^{-4}$) which certainly invalidated the results at the longer wave lengths. A somewhat improved cell was then made and the water was again distilled to obtain a conductivity of $\kappa = 1 \times 10^{-5}$ at the beginning and $\kappa = 3 \times 10^{-5}$ after several manipulations, including the filling of the cell. With such small samples it is difficult to obtain a higher purity than this. The conductivity still proved to be too high to give satisfactory results at 40 meters, but at 25° we found D_2/D_1, the ratio of the dielectric constant of H^2H^2O to that of H^1H^1O, to be 0.987 at 25 meters and 0.991 at 34 meters, while the value obtained with the more impure water at 25 meters was 0.993. The average of these three values, $D_2/D_1 = 0.990$ at 25°, may also be taken as the ratio at infinite wave length. The only attempt to obtain the temperature coefficient was made with the more impure water. At 10° (25 meters) we found $D_2/D_1 = 0.982$. Here as in all other cases we find the divergence between the two kinds of water increasing with diminishing temperature.

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RECEIVED OCTOBER 23, 1933 PUBLISHED NOVEMBER 7, 1933

NEW BOOKS

Principles of General Chemistry. By STUART R. BRINKLEY, Associate Professor of Chemistry, Yale University. Revised edition. The Macmillan Company, 60 Fifth Avenue, New York, 1933. x + 585 pp. Illustrated. 14.5 × 22.5 cm. Price, $3.50.

The text is intended for the use of college students who have had one year of preparatory chemistry in the lower schools. Because of this, Dr. Brinkley has been able to make some interesting changes in the arrangement of material. The Periodic System is placed in the second chapter where it can be used as a basis for the discussion of the modern theories of matter, which are developed in excellent style in the third chapter.

Acids are classified in groups and their salts are discussed with them in the manner used by many English writers. Metals also are classified and discussed in a very interesting way on the basis of the ores from which they are derived. This adds much to the unity of the chemical theory presented; it probably detracts from the value of the book as a reference for students.

In general the definitions are accurate and well stated. Some criticism might be made of the definition of secondary products of electrolysis on pp. 157 and 158, but the facts are presented correctly which is not the case in many otherwise excellent texts.

P. A. BOND

Jahrbuch der organischen Chemie. (Yearbook of Organic Chemistry.) Volume XIX, 1932. By Professor Dr. JULIUS SCHMIDT, Stuttgart. Verlagsbuchhandlung Franz Deuticke, Helferstorferstrasse 4, Wien, Austria, 1933. xx + 360 pp. 17 × 25.5 cm. Price, M. 36, öst. S. 54; bound, M. 39, öst. S. 58.50.

Although the author of the Jahrbuch died in March, the nineteenth volume has appeared in good time. Since Professor Schmidt had completed the manuscript before his death, the selection and the organization of the material are the same as in earlier volumes. The publisher and the son of the author, who supervised the publication, have succeeded in keeping it commendably free from annoying errors. They announce that they will do everything in their power to continue the Jahrbuch in the spirit of its founder.

E. P. KOHLER

BOOKS RECEIVED

September 15, 1933–October 15, 1933

DONALD M. LIDDELL AND GILBERT E. DOAN. "The Principles of Metallurgy." Th McGraw-Hill Book Co., Inc., 330 West 42d St., New York. 626 pp. $5.50.

"Mineral Resources of the United States." Part I. Metals. Bureau of Mines, U. S. Department of Commerce. Superintendent of Documents, Government Printing Office, Washington, D. C. 1142 pp. $1.50.

"Mineral Yearbook 1932–33." Bureau of Mines, U. S. Department of Commerce. Superintendent of Documents, Government Printing Office, Washington, D. C. 819 pp. $1.25.

JOURNAL OF THE
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VOLUME 55 DECEMBER, 1933 NUMBER 12

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY, ERLANGEN,[1] AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heats of Dilution of Aqueous Solutions of Zinc, Cadmium and Copper Sulfates and Sulfuric Acid at 25°

BY E. LANGE, J. MONHEIM AND A. L. ROBINSON

Introduction

This paper presents data on the heats of dilution of aqueous solutions of zinc, cadmium and copper sulfates and sulfuric acid at 25°, obtained with a sensitive differential adiabatic calorimeter already described.[2] Previous papers of this series have been concerned with the thermochemical properties of very dilute solutions of 1-1, 2-1 and 1-2 valence types of strong electrolytes. The present measurements, together with those on magnesium and calcium sulfates,[2c] afford a comparison of the integral heats of dilution of a series of 2-2 type salts with a common ion.

From the integral heats of dilution, obtained by extrapolation to infinite dilution from the lowest measured concentration, relative partial molal heat contents have been calculated and have been compared in the case of zinc sulfate with values obtained from e. m. f. measurements of galvanic cells.[3]

The inclusion in the heats of dilution at very low concentrations of heat effects due to the displacement of the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ is pointed out and discussed briefly.

Finally, certain "residual thermodynamic effects"[4] are presented graphically for the case of zinc sulfate.

Experimental

The apparatus and detailed procedure have been fully described elsewhere.[2] The left and right halves of the calorimeter (including the pipet volumes) contained 1650 ± 2 and 1665 ± 2 cc of water or solution, depending on whether a first or second dilution was being carried out. The pipets containing the solutions to be diluted had volumes of

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[1] No. 39 in a series of Thermochemical Communications.

[2] (a) Lange and Monheim, *Z. physik. Chem.*, **149A**, 51 (1930); (b) Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931); for further improvements see (c) Lange and Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

[3] Cowperthwaite, Thesis, Columbia University, New York City, 1930; La Mer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933).

[4] Schottky, "Thermodynamik," Julius Springer, Berlin, 1929; Lange and Hammerschmid, *Z. physik. Chem.*, **160A**, 445 (1932).

24.16 ± 0.02 (left) and 24.41 ± 0.02 cc. (right). The end concentration of a first dilution from a given initial concentration was practically the same as the end concentration of a second dilution made from an initial concentration equal to one-half the first initial concentration (see Table I), thus permitting all data for a given electrolyte to be consistently plotted together and extrapolated to the reference state of infinite dilution.[5]

The zinc, cadmium and copper sulfates used were recrystallized de Haën preparations furnished with a certificate of guaranty; the sulfuric acid solutions were made up from a "Fixanal-Substanz" 0.1 *N* solution (de Haën). All solutions were prepared on a volume basis. To avoid possible heat effects caused by hydrolysis in the case of the zinc and cadmium sulfates[6] both the solutions to be diluted and the dilution water were slightly acidified with sulfuric acid (3×10^{-6} *N*).[7]

Results

The first two columns of Table I give the initial and end concentrations of a dilution, respectively. The third column of the table gives the heat effects of individual measurements and the fourth column gives the average of the individual measurements. In Fig. 1 the data of Table I are plotted against the square root of the molality (where necessary the concentrations given on a volume basis have been calculated to molalities using density data taken from "International Critical Tables" and the Landolt-Börnstein "Tabellen"). The individual points lie well on the smooth curves drawn and below values of $m^{1/2}$ of about 0.05 the curves are straight lines within the limits of the experimental error. The curves have been extrapolated linearly on the assumption that the observed slopes remain constant to infinite dilution.[8] This extrapolation permits the values of the integral

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(5) Objections raised against the method of extrapolation [La Mer and Cowperthwaite, THIS JOURNAL, **54**, 4114 (1932)] were based on a misunderstanding and have been withdrawn [La Mer and Cowperthwaite, *ibid.*, **54**, 4754 (1932)].

(6) Dupont, *Compt. rend.*, **192**, 1643 (1931); Čupr, *Z. anorg. allgem. Chem.*, **198**, 310 (1931); Kolthoff and Kameda, THIS JOURNAL, **53**, 832 (1931); Denham and Marris, *Trans. Faraday Soc.*, **24**, 510 (1928).

(7) There is no reason to believe that the heats of dilution in pure water and in this very dilute sulfuric acid solution differ appreciably. The heats of dilution of potassium chloride in 15% aqueous sucrose solution and 5% aqueous urea solution [(Lange and Robinson, THIS JOURNAL, **52**, 4218 (193 differ only slightly from the values obtained in pure water despite the large differences that might be expected in view of the different dielectric properties of these solutions.

(8) That this assumption is subject to certain reservations is shown by measurements of E. Lange and H. Streeck now in progress. At very great dilutions the actual heats of dilution of salts seem to show an additional *positive* effect. Theoretically this effect is to be expected. The dilution water assumed to be pure and neutral, contains a greater concentration of electrolyte after the dilution process than before. From the law of mass action $a_{H^+}a_{OH^-}/a_{H_2O} = K$ and since the activity of the water is practically constant at these very small electrolyte concentrations, it follows that $c_{H^+}\gamma_{H^+}c_{OH^-}\gamma_{OH^-} = k$. Since with increasing electrolyte concentration the activity coefficients ($\gamma_{H^+}\gamma_{OH^-}$) decrease, the ion product must increase so that, accompanying the exothermal dilution process, there is an endothermal dissociation of water. This is a typical "secondary salt effect." As long as the final salt concentration of a dilution experiment is greater than about 10^{-4} *M* this endothermal effect is negligible in comparison with the exothermal interionic effects. At greater dilutions, however, the amount of diluting water is so great and the interionic effect is so small that the increased dissociation of the water finally determines the sign and magnitude of the actual heat of dilution.

The displacement of the water equilibrium influences the actual heats of dilution of acids (or bases) to an even greater extent. Due to the repression of the ionization of the assumed pure and neutral diluting water by the acid solution being diluted a heat of neutralization is evolved. The effect is only about 1.4×10^{-3} calorie per liter of water but this is sufficient to cause a galvanometer deflection of about 2 mm. in the sensitive calorimeter used in these measurements. The effect was observed, but not accounted for, in some unpublished measurements of the heat of dilution of hydrochloric acid solutions heat of dilution for a given concentration to be read from the curves. The measured heats of dilution are of course so-called intermediate heats of dilution. It is estimated that the linear extrapolation introduces an uncertainty of ±5 calories into the values of the integral heat of dilution (excluding effects due to the displacement of the water equilibrium).[8] The

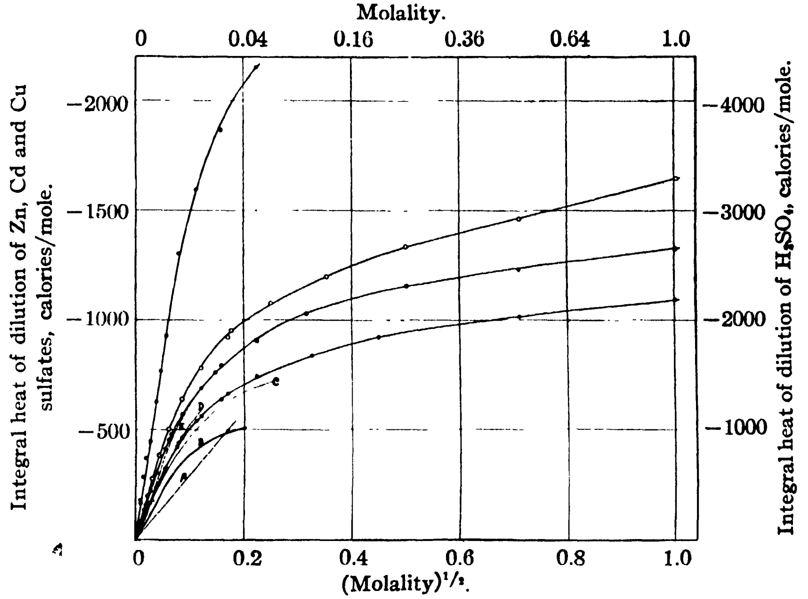

Fig. 1.—Integral heats of dilution at 25°: ○, $CdSO_4$; ◑, $CuSO_4$; ⊖, $ZnSO_4$; ●, H_2SO_4. A, Debye–Hückel limiting law; B, theoretical 2-2 type ("a" = 3.6 Å.), Lange–Meixner equation; C, $MgSO_4$; D, $CaSO_4$; E, $ZnSO_4$ (La Mer and Cowperthwaite).

roducibility of the results is indicated in column 5 of Table I. Systematic errors entering into all the measurements are the usual errors of calorimetric procedure and are estimated to be less than 1% when the initial oncentration of a dilution is greater than 0.00625 N and less than 1.5% for easurements starting at lower initial concentrations. Systematic errors ue to adsorption processes have repeatedly been shown to be absent. The possibility of heat leakage through the short 1500 junction thermopile and its effect on the accuracy of the measurements have been considered[2a] in detail. To answer the objection that might be raised that the initial and final temperatures are not the same and that the measurements are not

by A. L. Robinson in 1930. Measurements with sulfuric acid solutions by J. Monheim with initial concentrations of M/640, M/1280 and M/2560 show an increasingly steeper course of the intermediate heat of dilution curve with increasing dilution with a slope several times as great as in the region of proportionality with $m^{1/2}$. These measurements are not included in Table I but will be referred to in a future publication which will also present the measurements of Lange and Streeck mentioned above.

The linear extrapolation of the curves of Fig. 1 probably represents therefore only that part of the actual (observed) heat of dilution for which the interionic forces are responsible.

TABLE I

MEASURED HEATS OF DILUTION AT 25°

Init. concn., mole/liter	End concn., mole/liter	ΔH, calories/mole individual meas.		Av. ΔH^c cal./mole
Zinc Sulfate				
1.0	0.01465	−641.5	640.3[b]	641.7 ± 1.3[a]
		640.2	644.6	
	0.02908	−518.5		518.5
0.5	0.007323	−668.0	668.0	668.0
	0.01454	−546.8	546.4	546.6 ± 0.2
0.2	0.002929	−714.2	712.2	713.0 ± 0.9
		711.4	714.0	
	0.005816	−599.5	597.6	598.3 ± 0.9
		596.8	599.4	
0.1	0.001465	−716.0	718.2	717.1 ± 1.1
	0.002908	−615.8	613.8	614.8 ± 1.0
0.05	0.0007323	−688.0	686.0	687.0 ± 1.0
	0.001454	−603.8	603.6	603.7 ± 0.1
0.025	0.0003661	−619.6	618.0	618.8 ± 0.8
	0.0007269	−561.2	558.8	560.0 ± 1.2
0.0125	0.0001831	−545.7	545.5	545.6 ± 0.1
	0.0003635	−502.3	506.2	504.2 ± 2.0
0.00625	0.00009153	−463.0	463.7	463.4 ± 0.4
	0.0001817	−422.2	428.8	425.5 ± 3.4
0.003125	0.00004577	−326.8	336.1	331.5 ± 4.6
	0.00009086	−330.3	325.4	327.9 ± 2.5
Cadmium Sulfate				
1.0	0.01465	−1041	1036	1039 ± 1.7
		1038	1041	
	0.02908	−868.4	875.4	871.9 ± 3.5
0.5	0.007323	−984.0	985.8	984.9 ± 0.9
	0.01454	−816.2	814.6	815.4 ± 0.8
0.25	0.003661	−1001	994	997.5 ± 3.3
	0.007269	−836.4	832.1	834.3 ± 2.2
0.125	0.001831	−988.0	979.2	983.6 ± 4.4
	0.003635	−838.6	832.6	835.6 ± 3.0
0.0625	0.0009153	−961.8	962.0	961.9 ± 0.1
	0.001817	−836.0	836.2	836.1 ± 0.5
0.03125	0.0004577	−891.6	900.6	896.1 ± 4.5
	0.0009086	−804.8	810.2	807.5 ± 2.7
0.01	0.0002634	−678		678
	0.000520	−603		603
Copper Sulfate				
1.0	0.01465	−764.4	763.5	764.1 ± 1.1
		766.2	762.4	
0.5	0.007323	−796.1	797.6	796.9 ± 0.7
	0.01454	−651.6	655.5	653.6 ± 1.9
	0.02165	−567.7	569.5	568.6 ± 0.9

TABLE I (*Concluded*)

Init. concn., mole/liter	End concn., mole/liter	ΔH, calories/mole individual meas.	Av. ΔH^c cal./mole
0.25	0.003661	−845.8 843.4	844.3 ± 0.9
		843.7	
	0.007269	−704.4 703.4	703.9 ± 0.5
0.1	0.001465	−869.6 871.4	870.5 ± 0.9
	0.002908	−743.4 741.4	742.4 ± 1.0
	0.004332	−661.6 661.4	661.5 ± 0.1
0.05	0.0007323	−816.4 816.6	816.5 ± 0.1
	0.001454	−718.4 720.6	719.5 ± 1.1
0.025	0.0003661	−757.7 755.4	756.9 ± 6.1
		768.2 746.2	
	0.0007269	−638.8 682.8	682.0 ± 8.0
0.0125		695.0 666.2	
	0.0001831	−670.4 662.0	666.9 ± 6.3
		668.4 667.8	
		680.8 651.8	
	0.0003635	−628.2 617.2	
0.00625		616.2 619.4	
		627.2 603.8	618.7 ± 6.0
	0.00009153	−544.0 548.0	553.3 ± 6.2
		562.3 558.9	
	0.0001817	−524.0 525.8	524.1 ± 2.4
0.003125		527.4 519.2	
	0.00004577	475 422 451	449 ± 17.9
	0.00009086	440 410 427	426 ± 10.1
		Sulfuric Acid	
0.05	0.0007323	−3417 3380	3410 ± 14.8
		3432 3412	
	0.001454	−3050 3027	3048 ± 9.2
		3058 3058	
	0.002164	−2781 2758	2770 ± 12
0.025	0.0003661	−3082 3089	3086 ± 3
	0.0007269	−2839 2832	2836 ± 3.5
0.0125	0.0001831	−2637 2609	2623 ± 14
	0.0003635	−2462 2442	2452 ± 10
0.00625	0.00009153	−2164 1945	2055 ± 110
	0.0001817	−1996 1875	1936 ± 60
0.003125	0.00004577	−1662 1760	1711 ± 49
	0.00009086	−1479 1554	1517 ± 38

[a] Probable error, exclusive of systematic errors. [b] Negative values denote heat evolved; these values are given with too great precision to facilitate the plotting of the data and the calculation of the probable error. [c] $-V_{m_{\text{Anf}}m_{\text{End}}}$ in the German papers of this series.

therefore truly isothermal, it may be pointed out that the construction of the calorimeter on the differential principle permits the compensation of any temperature change produced by the dilution process in one half of the calorimeter by electrical heating in the other half. The m perature change produced by any of the dilution experim data are presented in Table I was only about 0.014° (in r considerably less); since this is probably within the limit of ordinary thermostatic control the method might be referred to as "adiabatic-isothermal" calorimetry.[9]

In Fig. 1 are also shown the results of Lange and Streeck for calcium and magnesium sulfates. The results of La Mer and Cowperthwaite[3] obtained from the temperature coefficient of the e. m. f. of the cell Zn-Hg (two phase)/$ZnSO_4(m)$, $PbSO_4(s)$/Pb-Hg (two phase) are also represented graphically in Fig. 1.

In Table II are given the values for the integral heat of dilution of zinc, cadmium and copper sulfates (to $m = 1$) and sulfuric acid (to $m = 0.05$) as read from the extrapolated curves of Fig. 1. Considering the precision of the measurements, possible systematic errors and the error introduced by the extrapolation to infinite dilution it is estimated that these values are accurate to ±10 calories.

The relative partial molal heat contents of electrolyte and water ($\bar{L}_2$ and $\bar{L}_1$) have been calculated for the same concentration range from the expressions[10]

$$\bar{L}_1 = \frac{m^{3/2}}{2(55.508)}\,\frac{d}{dm^{1/2}}\,(\Delta H_\infty) \text{ and } \bar{L}_2 = -\Delta H_\infty - \frac{m^{1/2}}{2}\,\frac{d}{dm^{1/2}}\,(\Delta H_\infty)$$

TABLE II

INTEGRAL HEATS OF DILUTION AT 25°

(Molality)$^{1/2}$	ΔH_∞,[a] calories/mole salt ZnSO$_4$	CdSO$_4$	CuSO$_4$	(Molality)$^{1/2}$	ΔH_∞, calories/mole H$_2$SO$_4$
0.01	− 76	− 110	− 97	0.01	− 327
.02	− 152	− 220	− 194	.02	− 655
.04	− 298	− 426	− 380	.04	−1304
.06	− 421	− 594	− 536	06	−1946
.08	− 526	− 733	− 653	.08	−2510
.1	− 606	− 847	− 748	.1	−2960
.15	− 756	−1058	− 920	.12	−3300
.2	− 851	−1190	−1047	.14	−3580
.3	− 978	−1364	−1218	.16	−3815
.4	−1069	−1498	−1318	.18	−3997
.5	−1129	−1601	−1385	.20	−4150
.6	−1175	−1675	−1431	.22	−4272
.7	−1215	−1751	−1476		
.8	−1250	−1824	−1517		
.9	−1284	−1898	−1554		
1.0	−1314	−1973	−1590		

— Vm in the German papers of this series.

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(9) Any changes in the heat of dilution due to these small temperature changes are negligible.

(10) Rossini, *Bur. Standards J. Research*, **6**, 799 (1931).

the required slopes being obtained graphically from a large scale plot of Fig. 1 or by the use of the Lagrange interpolation formula.[11] Table III gives the values of $\overline{L}_1$ and $\overline{L}_2$ so obtained and Fig. 2 shows a plot of these values against $m^{1/2}$

TABLE III

RELATIVE PARTIAL MOLAL HEAT CONTENTS AT 25°

	$\overline{L}_1$[a] cal./mole H_2O				$\overline{L}_2$,[a] cal./mole electrolyte			
(Molality)$^{1/2}$	$ZnSO_4$	$CdSO_4$	$CuSO_4$	H_2SO_4	$ZnSO_4$	$CdSO_4$	$CuSO_4$	H_2SO_4
0.01	-0.0_468	-0.0_499	-0.0_488	-0.0_329	114	163	145	490
.02	$-.0_354$	$-.0_379$	$-.0_370$	− .0024	227	330	291	982
.04	− .0041	− .0064	− .0050	− .0176	440	607	553	1958
.06	− .0104	− .0142	− .0132	− .0615	620	825	746	2894
.08	− .0192	− .0276	− .0234	− .112	723	979	861	3478
.1	− .033	− .048	− .039	− .181	790	1111	965	3965
.12				− .230				4188
.14				− .314				4470
.15	− .066	− .101	− .085		918	1306	1150	
.16				− .376				4631
.18				− .449				4767
.2	− .117	− .188	− .165	− .497	1014	1420	1277	4840
.22				− .571				4928
.3	− .271	− .347	− .316		1145	1582	1410	
.4	− .416	− .62	− .47		1214	1712	1472	
.5	− .59	− .96	− .65		1256	1814	1522	
.6	− .79	−1.48	− .88		1301	1908	1573	
.7	−1.04	−2.22	−1.23		1342	2007	1618	
.8	−1.43	−3.28	−1.68		1380	2106	1668	
.9	−1.96	−4.72	−2.28		1424	2212	1721	
1.0	−2.76	−6.48	−3.25		1468	2333	1773	

[a] $\mathfrak{W}_1$ and $\mathfrak{W}_2$ in the German papers of this series.

Discussion

With the limits of experimental error the measured (intermediate) heats of dilution are proportional to $m^{1/2}$ below about 0.001 *M*. This proportionality (but not the value of the factor of proportionality) is in agreement with the limiting Debye–Hückel law. Although the extended theory[12] requires that the heats of dilution fuse into the limiting law straight lines at very low concentrations ($\Delta H_\infty = -2440\, c^{1/2}$ for 2–1 and 1–2 types and $-3765\, c^{1/2}$ for the 2–2 type) these measurements, which extend to 0.00005 *M*, give no definite indication of the "hump" found by La Mer and Cowperthwaite[8] for zinc sulfate and by La Mer and Parks[13] for cadmium sulfate at 12.5°. The data have therefore, as explained above,[8] been extrapolated linearly to infinite dilution. The individuality of the slopes persists to the lowest measured concentration; this has already been repeatedly

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(11) Running, "Empirical Formulas," John Wiley and Sons., Inc., New York City, 1917.

(12) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

(13) La Mer and Parks, THIS JOURNAL, **53**, 2040 (1931).

emphasized for 1–1, 2–1 and 1–2 types of electrolytes.[14] The values of the slopes (below 0.001 *M*) are −32,700 for sulfuric acid, −10,800 for cadmium sulfate, −9500 for copper sulfate, −7500 for zinc sulfate and −7300 for calcium sulfate and magnesium sulfate.[2c] The limiting slope

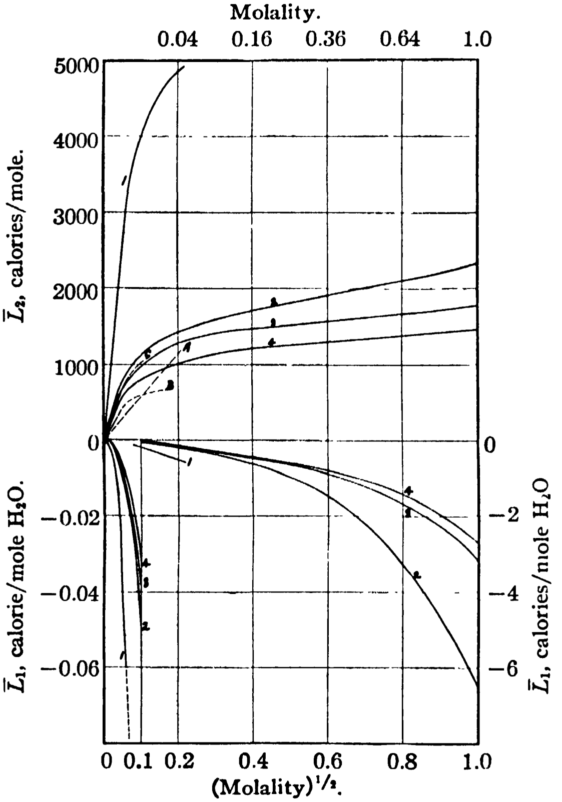

Fig. 2.—Relative partial molal heat contents at 25°: 1, H_2SO_4; 2, $CdSO_4$; 3, $CuSO_4$; 4, $ZnSO_4$. A, Debye–Hückel limiting law; B, theoretical 2-2 type ("*a*" = 3.6 Å.), Lange–Meixner equation; C, $ZnSO_4$ (La Mer and Cowperthwaite).

for sulfuric acid, if it is to be considered a 1–2 type electrolyte, is to be compared with the values found for the alkali sulfates,[2e] which range from −2200 for lithium sulfate to −1800 for cesium sulfate. It is quite possible that below 0.00005 *M* the individual curves fuse into the proper type curve but as far as the heats of dilution have been carried at present no definite confirmation of this suggestion has been found.

There are considerable differences between the values of ΔH_∞ and $\bar{L}_2$

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(14) In general activity coefficients determined from freezing point or e. m. f. data do not show the same individuality or "degree of resolution" shown by the heats of dilution. This is perhaps partly because of the lower accuracy of the former type of measurement.

for zinc sulfate reported in this paper and those determined by La Mer and Cowperthwaite by application of the Gibbs–Helmholtz equation. A comparison of results reported in previous papers of this series with $\bar{L}_2$ values computed from e. m. f. measurements shows poor agreement in several other instances.[15] There is no theoretical ground for expecting the two methods to yield different results.[16] It is possible that the discrepancies are due to the usual difficulties encountered in obtaining accurate e. m. f. values in addition to the necessity for working over a wide temperature range and the uncertainty involved in the extrapolation from the lowest measured concentration (calorimetric measurements have been carried to lower concentrations) to infinite dilution.

In Fig. 1 the broken straight line represents the integral heat of dilution of a 2–2 type electrolyte as given by the limiting form of the Debye–Hückel theory.[17] Gatty[18] and Scatchard[19] have recently shown the necessity for the term in $\mathrm{d}V/\mathrm{d}T$.

$$\Delta H_\infty = \frac{0.239\ N^{3/2}\epsilon^3}{10^7\ D^{3/2}T^{1/2}}(\pi/1000\,k)^{1/2}(\Sigma\nu_i z_i^2)^{3/2}(1 + T/D\ \mathrm{d}D/\mathrm{d}T + T/3V\ \mathrm{d}V/\mathrm{d}T)c^{1/2}\ \text{cal./mole} \qquad (1)$$

Equation (1) becomes $\Delta H_\infty = -3765\ c^{1/2}$ for a 2–2 type electrolyte when Wyman's[20] data for the dielectric properties of water are used and the term in $\mathrm{d}V/\mathrm{d}T$ is placed equal to 0.015.[21] Figure 1 also shows the integral heat of dilution of a 2–2 electrolyte with an "a" parameter equal to 3.6 Å.[22] as computed from the equation of Lange and Meixner[23] which is based on the extended Debye–Hückel theory[12]

$$\Delta H_\infty = -\frac{1143\,z^2}{a}\frac{x}{1+x} + \frac{56.92(z^2)^3}{a^3}10^3X_3(x) + \frac{28.35(z^2)^5}{a^5}10^5X_5(x)\ \text{cal./mole} \qquad (2)$$

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(15) Sodium chloride (e. m. f.) Harned and Nims, THIS JOURNAL, **54**, 423 (1932); (calorimetric) Robinson, *ibid.*, **54**, 1311 (1932), and Young and Vogel, *ibid.*, **54**, 3030 (1932); potassium bromide (e. m. f.), Pearce and Hart, *ibid.*, **43**, 2483 (1921), (calorimetric) Hammerschmid and Robinson, *ibid.*, **54**, 3120 (1932). A comparison of $\bar{L}_2$ values for cadmium sulfate at 12.5° in the concentration range 0.1–0.0005 M as determined by La Mer and Parks (e. m. f.), *ibid.*, **53**, 2040 (1931), and Plake (calorimetric), *Z. physik. Chem.*, **162A**, 257 (1932), also shows considerable differences.

(16) The relative partial molal heat contents of aqueous hydrochloric acid solutions as determined from the temperature coefficients of the cells $^1/_2H_2/HCl(m)/HgCl(s)/Hg$ [Ellis, THIS JOURNAL, **38**, 737 (1916)]; Noyes and Ellis, *ibid.*, **39**, 2532 (1917), agree with calorimetric measurements (Robinson, unpublished data) to better than one per cent. in the range 0.05–0.001 M.

(17) Debye and Hückel, *Physik. Z.*, **24**, 193 (1923).

(18) Gatty, *Phil. Mag.*, **11**, 1082 (1931).

(19) Scatchard, THIS JOURNAL, **53**, 2037 (1931).

(20) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(21) The term $T/3V\ \mathrm{d}V/\mathrm{d}T$ is an individual quantity (specific for each electrolyte) in an otherwise non-individual expression. However an inspection of the available data on the thermal expansion of 2–2 type electrolyte solutions (Landolt-Börnstein "Tabellen") shows that below 0.02 M the term has a value of 0.015 for magnesium sulfate, 0.0135 for zinc sulfate and 0.017 for copper sulfate so that a mean value of 0.015 can be used with sufficient exactness.

(22) This value of "a" has been selected for computation and plotting because La Mer and Cowperthwaite found "a" for zinc sulfate to be 3.64 Å. at 25° (in fact they found "a" to be practically temperature independent between 0 and 37.5°) and La Mer and Parks [THIS JOURNAL, **53**, 2040 (1931)] obtained a value of 3.6 Å. for cadmium sulfate (also from e. m. f. measurements).

(23) Lange and Meixner, *Physik. Z.*, **30**, 670 (1929).

In Equation (2) the coefficients have been calculated using Wyman's dielectric constant data.[24]

In Fig. 2 are also shown the limiting Debye–Hückel law for $\bar{L}_2$ of a 2–2 type electrolyte, $\bar{L}_2 = 5700\ c^{1/2}$,[25] and the partial molal heat content of a 2–2 type electrolyte with an "a" parameter equal to 3.6 Å.[26] and the results of La Mer and Cowperthwaite for $\bar{L}_2$ of zinc sulfate.

La Mer and Cowperthwaite and La Mer and Parks have interpreted e. m. f. measurements as indicating that $\mathrm{d}a/\mathrm{d}T$ is practically zero for zinc and cadmium sulfates. La Mer and Cowperthwaite[3] suggest that since $\mathrm{d}a/\mathrm{d}T$ is equal to zero, the individuality of the heats of dilution at low concentrations is to be attributed to the specific concentration dependence of D and perhaps V. Lange and Hammerschmid[4] have pointed out that the differences in the values of $T/3V\ \mathrm{d}V/\mathrm{d}T$ for salts of the same valence type cannot contribute more than one or two per cent. to the individuality of ΔH_∞ at low concentrations, an amount not detectable experimentally. Since La Mer and Cowperthwaite used the dielectric constant of pure water in their calculations of $\mathrm{d}a/\mathrm{d}T$ it is difficult to see how any conclusion can be drawn as to the specific concentration dependence of D and $\mathrm{d}D/\mathrm{d}T$ from the result $\mathrm{d}a/\mathrm{d}T = 0$, obtained with the above premise. The heats of dilution of potassium chloride in aqueous sucrose and urea solutions[27] differ only slightly from the values obtained in pure water in spite of the large differences that might be anticipated from a consideration of the different dielectric properties of these media. If reliable measurements of D and $\mathrm{d}D/\mathrm{d}T$ for electrolyte solutions were available it might be possible to estimate the contributions of these various specific factors to the individuality of the heats of dilution.

However, that the "a" values for zinc sulfate and cadmium sulfate are practically the same (3.64 and 3.6 Å.) as found by La Mer and Cowperthwaite and La Mer and Parks does not agree with our results. Assuming that $\mathrm{d}a/\mathrm{d}T$ is equal to zero and that D and $\mathrm{d}D/\mathrm{d}T$ are the same as for pure water both the Scatchard and Lange–Meixner equations applied to these measurements indicate that the "a" values for zinc sulfate and cadmium sulfate differ considerably at 25°. A rough computation shows that if the difference in the observed ΔH_∞ values for these two salts is to be attributed

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(24) $x = \kappa a$, $\kappa = 0.3293\ c^{1/2}/10^8$ and the values for $X_3(x)$ and $X_5(x)$ have been taken from the tables prepared by Gronwall, La Mer and Sandved. The equation of Scatchard [Ref. 19 (equation (7), p. 2038)] containing the term in d ln V/d ln T would give a curve lying slightly above the Lange–Meixner curve. The heat of dilution according to Scatchard has not been calculated since the difference between the values given by the two equations is probably less than 10%. Moreover, both equations converge rather poorly; the term in $X_5(x)$ contributes as much as 25% of the total to the calculated ΔH_∞ values (Lange–Meixner) at 0.002 M and $X_7(x)$ and $X_9(x)$ have not been computed.

(25) Bjerrum, *Z. physik. Chem*, **119**, 145 (1926). This expression lacks the term in $\mathrm{d}V/\mathrm{d}T$ (Refs. 18, 19).

(26) $\bar{L}_2$ according to the Lange–Meixner equation has been calculated from the plot of ΔH_∞ (as calculated from equation (2)) against $m^{1/2}$, determining the slope of this curve and substituting in $\bar{L}_2 = -\Delta H_\infty - (m^{1/2}/2)(d/dm^{1/2})(\Delta H_\infty)$.

(27) Lange and Robinson, THIS JOURNAL, **52**, 4218 (1930).

solely to a difference in the "a" parameter then $a_{\mathrm{ZnSO_4}} - a_{\mathrm{CdSO_4}} \approx 1.5$ Å.

The observed initial slopes for the 2-2 type salts agree poorly with the value required by the limiting law. The agreement for 1-1, 2-1 and 1-2 types (except sulfuric acid) is much better.

According to the extended interionic attraction theory ΔH_∞ should be less negative as "a" increases in a series of electrolytes of the same valence type. If the values of "a" parallel the crystal radii of the variable ion in a series of salts with a common ion we should expect to find $a_{\mathrm{CaSO_4}} > a_{\mathrm{CdSO_4}} > a_{\mathrm{ZnSO_4}} > a_{\mathrm{MgSO_4}}$ with the position of $a_{\mathrm{CuSO_4}}$ uncertain.[28] On the basis of Equation (2) the results indicate $a_{\mathrm{CaSO_4,\,MgSO_4}} > a_{\mathrm{ZnSO_4}} > a_{\mathrm{CuSO_4}} > a_{\mathrm{CdSO_4}}$ below 0.001 M. The order of "a" as indicated by the heats of dilution of all 1-1, 2-1 and 1-2 type electrolytes investigated is that suggested by the order of the crystal ion radii. The order of the activity coefficients is not always the same.[29] The theoretical interpretation of this apparent anomaly is still obscure.

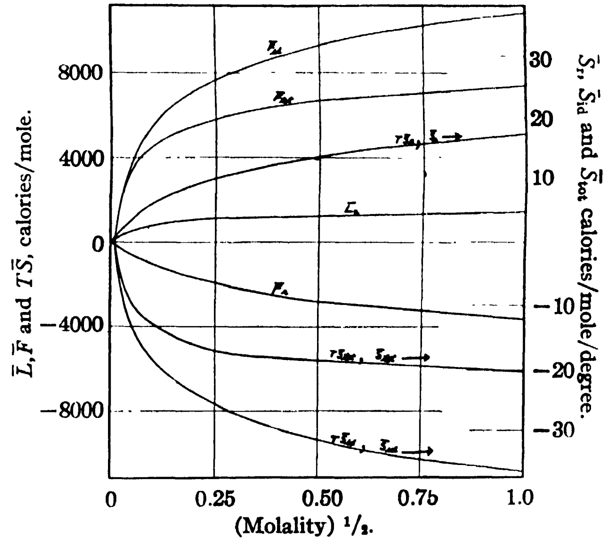

Fig. 3.—Partial molal quantities (real, ideal and total) of aqueous $ZnSO_4$ solutions at 25°.

In Fig. 3 are presented graphically the relative partial molal quantities $\bar{F}$, $\bar{S}$, $T\bar{S}$ and $\bar{L}$ for zinc sulfate for the concentration range of these measurements. The total partial molal quantities ($\bar{F}_{\mathrm{tot}}$, etc.) have been divided into their real ($\bar{F}_{\mathrm{r}}$, etc.) and ideal ($\bar{F}_{\mathrm{id}}$, etc.) parts, whereby[30]

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(28) Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo* **1**, *Mat-Naturv. Klasse*, 1926, No. 2; Pauling, THIS JOURNAL, **49**, 765 (1927).

(29) Lange and Streeck, *Naturwissenschaften*, **19**, 359 (1931).

(30) For a comparison of the terminology of this paper, which is that of Lewis and Randall ["Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923], and of the papers of this series published in German journals, which use the notation of Schottky,[4] see Lange and Hammerschmid.[4]

$$\bar{F}_{\text{id}} = 2RT \ln m \qquad \bar{F}_{\text{r}} = 2Rt \ln \gamma \qquad \bar{S}_{\text{id}} = -2\text{R} \ln m$$

$$\bar{S}_{\text{r}} = 2RT \text{d} \ln \gamma/\text{d}\, T - 2R \ln \gamma \qquad \bar{L}_{\text{r}} = \bar{L}_{\text{tot}} = -2RT^2 \text{d} \ln \gamma/\text{d}T$$

The $\bar{L}_{\text{tot}} = \bar{L}_{\text{r}}$ values are taken from Table III, the $\bar{F}_{\text{r}}$ values are calculated from the activity coefficients (γ) determined by Bray[31] and the $\bar{S}_{\text{r}}$ values are calculated from $\bar{S}_{\text{r}} = (\bar{L} - \bar{F}_{\text{r}})/T$. In Fig. 3 all total and ideal quantities are referred to the 0.0001 *M* solution. Of particular theoretical interest are the real quantities $\bar{L}$, $\bar{F}_{\text{r}}$, $T\bar{S}_{\text{r}}$ and $\bar{S}_{\text{r}}$, amounts absorbed in the transfer of one mole of zinc sulfate from the reference state of infinite dilution to a real solution of given concentration. The possible physical processes which determine the sign and magnitude of these effects have been discussed elsewhere.[4]

The experimental part of this work was kindly aided by the Notgemeinschaft of the German Sciences.

Summary

The heats of dilution of aqueous solutions of cadmium, copper and zinc sulfates (from 1 *M* to 0.00005 *M*) and sulfuric acid (from 0.05 *M* to 0.00005 *M*) have been measured calorimetrically at 25° and extrapolated to infinite dilution to obtain integral heats of dilution.

Additional heat effects accompanying the dilution of very dilute electrolyte solutions due to the displacement of the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ have been discussed.

Relative partial molal heat contents and, for zinc sulfate, other related partial molal quantities (real and ideal) have been calculated for the concentration range of the measurements.

PITTSBURGH, PA.

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(31) Bray, THIS JOURNAL, 49, 2372 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Dipole Moments of the Chlorobenzophenone Oximes

BY GEORGE S. PARSONS AND C. W. PORTER

Uncertainty concerning the mechanism of the Beckmann rearrangement makes it highly desirable to find some method, independent of the rearrangement, for determining the configurations of the isomeric oximes. A few attempts have been made to accomplish this by dipole moment measurements. Hassel and Naeshagen made the first study of this kind.[1] They used benzaldoxime and acetaldoxime in benzene solution but abandoned the plan on account of the tendencies of the oxime molecules to associate. Sutton and Taylor sought to overcome this difficulty by using the N-methyl ethers of oximes.[2] There is, however, the remote possibility that *cis–trans* isomerization occurs in the process of forming the N-ether. There is no strict guarantee that an ether corresponds in structure to the oxime from which it is derived.

We have measured the dipole moments of the *ortho* and *para* chlorobenzophenone oximes in dioxane—a solvent in which the free oximes have little tendency to associate. The two oximes derived from *m*-chlorobenzophenone were measured in benzene and in carbon tetrachloride before we found that dioxane was a better solvent. Since we do not intend to continue this work we include in this paper the average values of the dipole moments of the *meta* compounds as measured in benzene and carbon tetrachloride although there was evidence of association in both of these solvents and the numbers reported cannot be true values. For the purpose of this investigation the absolute values of the moments are not required. The point of interest is to find out which member of the pair of oximes has the higher moment.

The apparatus comprised a crystal controlled oscillator operating at a frequency of 500 kilocycles, another oscillator the frequency of which was determined by a fixed inductance and a precision variable condenser, a radio receiving set and a source of constant frequency sound waves. The method has been described in detail by Williams and Weissberger,[3] Smyth,[4] Zahn[5] and others.

Dioxane freezes at 11° and the oximes decompose rapidly above 50°. The available temperature range, therefore, was too narrow to permit a calculation of the dipole moment by elimination of the P_A and P_E factors by dielectric constant measurements at different temperatures. We used, therefore, the refractive indices of the solutions to supplement the polari-

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(1) Hassel and Naeshagen, *Z. physik. Chem.*, **4B**, 217 (1929).

(2) Sutton and Taylor, *J. Chem. Soc.*, 2190 (1931).

(3) Williams and Weissberger, THIS JOURNAL, **50**, 2332 (1928).

(4) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York.

(5) Zahn, *Phys. Rev.*, **24**, 400 (1924).

zation measurements and we assumed that in the equation $P = P_E + P_A + P_M$ the term P_A (atomic polarization) would be the same for each member of a pair of isomeric oximes. The refractive indices were measured with a Pulfrich refractometer which was kept at constant temperature by circulating water from a thermostat. The pycnometers used in the density measurements were brought to the same temperature by immersion in the same thermostat bath.

Our values for the dipole moments are as follows

o-Chlorobenzophenone oximes: α-form (m. p. 131°) 161 $\times 10^{-18}$, β-form (m. p. 96–97°) 161 $\times 10^{-18}$ e. s. u.

p-Chlorobenzophenone oximes: α-form (m. p. 162–164°) 2.320 $\times 10^{-18}$, β-form (m. p. 91–92°) 2.381 $\times 10^{-18}$ e. s. u.

m-Chlorobenzophenone oximes: α-form (m. p. 132–133°) 1.50 $\times 10^{-18}$, β-form (m. p. 105–106°) 1.61 $\times 10^{-18}$ e. s. u.

In all cases where members of the isomeric pairs show different polarizations, the higher melting form has the lower dipole moment and in every case the high-melting form rearranges to yield an amide in which the unsubstituted phenyl group is found attached to the nitrogen atom.

These results do not give an unambiguous answer to the question of oxime structures. The measured moment is the vector sum of several moments in the molecule. The difference between the values for the two members of a pair of oximes may be attributed definitely to the *cis* and *trans* configurations but we do not know the direction of the resultant of the vectors between the nitrogen and oxygen atoms and between the hydrogen and oxygen atoms. If the hydroxyl group as a whole is positive with respect to the nitrogen atom, these measurements support the Meisenheimer mechanism of the Beckmann rearrangement.[6] If the negative end of the resultant dipole is toward the hydroxyl group, these results support the original view of Hantzsch.[7]

Summary

The dipole moments of the six oximes obtainable from monochlorobenzophenone have been measured with sufficient accuracy to determine the relative values in the three pairs of *cis–trans* isomers. Within the limits of accuracy obtainable with our equipment the two *ortho* compounds have identical moments. The higher melting forms of the *meta* and *para* compounds have the lower dipole moment.

The chlorinated phenyl group shifts to the nitrogen atom when the low-melting form is subjected to the Beckmann rearrangement. The unsubstituted phenyl group migrates when the high-melting oxime undergoes the Beckmann change.

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(6) Meisenheimer, *Ber.*, **54**, 3206 (1921).

(7) Hantzsch, *ibid.*, **24**, 22 (1891).

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, YALE UNIVERSITY]

The Equilibrium between Carbon Monoxide, Hydrogen, Formaldehyde and Methanol.[1] I. The Reactions $CO + H_2 \rightleftharpoons HCOH$ and $H_2 + HCOH \rightleftharpoons CH_3OH$

BY ROGER H. NEWTON AND BARNETT F. DODGE

Introduction

Because of its great industrial importance the direct synthesis of formaldehyde from carbon monoxide and hydrogen has attracted the attention of investigators for many years. (All investigations in which synthesis was attempted in the presence of special forms of energy such as electrical discharges, or ultraviolet radiation, are beyond the scope of this paper; only the purely thermal synthesis will be considered.) In spite of all the attempts that have been made to bring about this reaction there appear to be no quantitative results of any value and there is not even a qualitative agreement on the possibility of the synthesis. The successful accomplishment of the methanol synthesis at high pressures has aroused new interest in the problem. In the published investigations of the methanol synthesis there has been practically no mention of formaldehyde and only one paper giving any data. Several recent patents claim good yields of formaldehyde in high pressure synthesis from carbon monoxide and hydrogen but the claims are not supported by any experimental facts.

The failure of most investigators to obtain more than a trace of formaldehyde (and even that doubtful in most cases) may be due either to an unfavorable equilibrium or to lack of the proper catalyst. Some recent investigators[2] have inclined to the latter view, but the preponderance of evidence points to a very unfavorable equilibrium.

There are no low temperature thermal data on formaldehyde and so the third law of thermodynamics cannot be applied to the calculation of an equilibrium constant. Parks and Huffman[3] have recently presented an equation for the free energy of formation of formaldehyde, based on a rough analogy between the structure of formaldehyde and ethylene. Combining this with their value for the free energy of carbon monoxide, the value of Kp for the formaldehyde synthesis reaction may be calculated. A value of 5×10^{-6} is obtained at 250°. The Nernst approximation, which is often surprisingly accurate, also predicts a very small equilibrium constant for this reaction but this prediction is rather uncertain because of the conflicting data on the heat of combustion of monomolecular formaldehyde gas. Using the heat of combustion of formaldehyde gas determined by von Wartenburg and Lerner-Steinberg[4] ($\Delta H = -134{,}700$) and other recent thermal data, the predicted value of the equilibrium constant at 250° is 0.5×10^{-6}. It is to be noted that small errors in the heat of combustion of formaldehyde will make a very large error in the calculated Kp because the heat of reaction is less than one-hundredth of the heat of combustion. Hence it is necessary to make actual equilibrium measurements if anything approaching a trustworthy value for Kp is to be obtained.

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[1] This paper is based on a Dissertation presented by R. H. Newton in June, 1933, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. It is also a revision of a preliminary paper presented before the Division of Physical and Inorganic Chemistry at the Denver meeting, August, 1932.

[2] Bone, *Trans. Inst. Chem. Engrs.* (London), **8**, 98 (1930); Frolich, *Ind. Eng. Chem.*, **23**, 111 (1931).

[3] "Free Energies of Some Organic Compounds," A. C. S. Monograph No. 60.

The reaction $CH_3OH \rightleftharpoons HCOH + H_2$ is the basis of the commercial process for formaldehyde manufacture and yet there are no reliable data on the equilibrium conditions. It is also to be noted that a combination of this reaction with the methanol synthesis reaction, for which fairly reliable equilibrium data exist, enables one to secure a check on the directly-determined value for the equilibrium constant of the formaldehyde synthesis reaction.

It is the belief of the authors that this paper presents the first reliable experimental data on the equilibrium conditions in those two reactions.

Review of Previous Work

Synthesis of Formaldehyde.—A number of investigators[5] have attempted to synthesize formaldehyde over catalysts at atmospheric and slightly elevated pressures. The results are conflicting but the general conclusion is that either a very slight trace of formaldehyde or none at all results when carbon monoxide and hydrogen are passed over a catalyst.

Formaldehyde has not been reported in most of the high pressure synthesis from carbon monoxide and hydrogen but Morgan, Hardy and Proctor,[6] have definitely identified formaldehyde in the products resulting from the reaction of carbon monoxide and hydrogen at high pressure over Cr–Mn–Rb catalysts. Only 0.2% of the total carbon reacting appeared as formaldehyde at a temperature of 420° and a pressure of 200 atm.

It should be noted that many of the above-mentioned investigators were quite vague as to their methods of determining formaldehyde and none of them can be said to have obtained quantitative results for the equilibrium.

Decomposition of Formaldehyde.—There has been a vast amount of work on this subject. The conclusion reached by a number of the later investigators,[7] is that formaldehyde is almost completely decomposed at 1 atm. and at all temperatures above 150°. Ghosh and Chakravarty,

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(4) Von Wartenburg and Lerner-Steinberg, *Z. angew. Chem.*, **38**, 591 (1925).

(5) Jahn, *Ber.*, **22**, 989 (1889); Chapman and Holt, *J. Chem. Soc.*, **87**, 916 (1905); Gautier, *Compt. rend.*, **150**, 1564 (1910); Marshall and Stedman, *Trans. Roy. Soc. Can.*, [III] **17**, 53 (1923); Jaeger and Winkelmann, *Ges. Abhandl. Kenntnis Kohle*, **7**, 55 (1925); Sabalitschka and Harnisch, *Biochem. Z.*, **190**, 265 (1927); Neumann and Biljcevic, *Z. angew. Chem.*, **40**, 1469 (1927); Vogel, *Helv. Chim. Acta*, **11**, 370 (1928); Fischer and Jaeger, *Ges. Abhandl. Kenntnis Kohle*, **7**, 68 (1925).

(6) Morgan, Hardy and Proctor, *J. Soc. Chem. Ind.*, **51**, 1T (1932).

(7) Tropsch and Roelen, *Ges. Abhandl. Kenntnis Kohle*, **7**, 15 (1925); Marshall and Stedman, *loc. cit.*; Ghosh and Chakravarty, *Quart. J. Indian Chem. Soc.*, **2**, 142 (1925); Medvedev and Robinson, *Trans. Karpov. Chem. Inst.*, **3**, 54 (1924).

however, find *Kp* to be greater than 1.0 at all temperatures below 300° and it appears that their results are not above suspicion.

The Dehydrogenation of Methanol.—This has also been the subject of many investigations, and the results are conflicting. The interpretation of much of this work given by textbooks[8] is vague, particularly as regards temperature. The implication is that methanol may be appreciably dehydrogenated to formaldehyde at temperatures below 300°. Ghosh and Baksi reported almost complete conversion of methanol to formaldehyde at 200°[9] but this is at variance with nearly all other workers in this field.

The commercial process for manufacture of formaldehyde from methanol is essentially a dehydrogenation since an insufficiency of oxygen is used, but it is well known that temperatures above 400° and high space velocities are necessary for good yields. The data reported by LeBlanc and Plaschke[10] might enable one to estimate very roughly the equilibrium constant of the reaction.

Apparently the reverse reaction or hydrogenation of formaldehyde had not been studied quantitatively. Sabatier[8] states that it takes place readily over nickel even at as low a temperature as 90°. Fischer[11] refers briefly to experiments in which $H_2 + HCOH$ yielded considerable quantities of methanol at 400° and 100 atm.

Experimental Part

Analytical Methods.—Gas analyses were made on a U. S. Steel Corporation type of Orsat gas analysis apparatus provided with a mercury-sealed buret and a compensator for temperature and pressure changes. The percentage of illuminants was found to be negligible [illegible] the analysis was simplified by omitting this step. Carbon monoxide was determined by absorption in acid cuprous chloride, methane and hydrogen by slow combustion with a platinum spiral.

In the experiments on the hydrogenation of formaldehyde, the liquid product was analyzed for formaldehyde, methanol and methyl formate. Methyl formate was determined by saponification, the details of the method being worked out by a series of experiments on known amounts of pure methyl formate. Methanol and formaldehyde were found not to interfere with this determination. Methanol was determined by the method of Lockemann and Croner,[12] which is total oxidation with alkaline permanganate with subsequent correction for the amounts of formaldehyde and methyl formate found. The methyl formate equivalent of 1 cc. of 0.5 *N* permanganate was found to be the theoretical value of 0.00375 g. of methyl formate per cc. of permanganate used. In the case of formaldehyde, the theoretical equivalent was used. Formaldehyde was determined by the iodine method of Romijn.[13] According to the literature, methanol and methyl formate do not interfere, and this was found to be true as long as one was not

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(8) Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1922; Rideal and Taylor, "Catalysis in Theory and Practice," The Macmillan Co., New York, 1926; Hilditch, "Catalytic Processes in Applied Chemistry," D. Van Nostrand Co., New York, 1929.

(9) Ghosh and Baksi, *Quart. J. Indian Chem. Soc.*, **3**, 415 (1926).

(10) LeBlanc and Plaschke, *Z. Electrochem.*, **17**, 45 (1911).

(11) Fischer and Tropsch, *Ber.*, **56**, 2438 (1923).

(12) Lockemann and Croner, *Z. anal. Chem.*, **54**, 11 (1915).

(13) Romijn, *ibid.*, **36**, 18 (1897).

attempting to determine extremely small amounts of formaldehyde. Acetone, however, does interfere, but at concentrations above one part in 250,000 there is an opalescence due to iodoform, even in the presence of 10% methanol which was the maximum amount present in any of the solutions analyzed. An opalescence was not observed and so the absence of acetone was assumed. The methods were tested on the pure substances and on mixtures of all three and found to be accurate to about 2%.

In the experiments on direct synthesis of formaldehyde and methanol the amount of condensate was very much smaller and a more sensitive method for formaldehyde was necessary. It was found that by using *n*/100 iodine, the Romijn method could be made much more sensitive without appreciable loss in accuracy. In pure formaldehyde solutions, or in mixtures of formaldehyde and methyl formate, an accuracy of 2% could be obtained in solutions which contained only 0.20 mg. of formaldehyde. This method was found to be more sensitive than any of the colorimetric methods, since it was less affected by dilution. An extensive survey of the colorimetric tests for formaldehyde was made, and the morphine test of Bonnet[14] and the well-known Schiff's test were found the most sensitive and the most specific. Most of these tests are not suitable for quantitative determination since the colors are so readily affected by slight changes in conditions. Thus the morphine test was used qualitatively only, since the color was somewhat modified by the presence of methanol. The Schiff test was applied quantitatively, as it appeared to be unaffected by methanol or methyl formate, but it is somewhat less sensitive than the morphine test. Substances other than formaldehyde give a color, but a blue color appears to be specific.

Since very small amounts of formaldehyde had to be determined in the presence of relatively large amounts of methanol, it was necessary to examine carefully the question of interference by methanol. A large number of tests were made on methanol purified from traces of aldehydes by distillation from alkaline iodine solution, and from silver oxide and it was definitely established that 0.01 *N* iodine does react with methanol, the extent of reaction being a function of time and iodine concentration. By reducing the time to the minimum found necessary for complete reaction with formaldehyde (15 minutes) and using only a small excess of iodine solution (about 10%), the percentage error was minimized. The following tabulation, giving results on the analysis of known mixtures, shows the extent of the interference.

TABLE I

INTERFERENCE OF METHANOL WITH THE 0.01 *N* IODINE METHOD FOR FORMALDEHYDE

MeOH taken, g.	0.16	0.16	0.16	0.32	0.32	0.32	0.64	0.64	0.64
HCHO taken, mg.	.00	.81	1.61	.00	.81	1.61	.00	.81	1.61
HCHO found, mg.	.10	.83	1.66	.09	.86	1.68	.18	.88	1.72
Error, mg.	.10	.02	.05	.09	.05	0.07	.18	.07	0.11

It is evident that the error is less than 10% when the amount of formaldehyde is 1.0 mg. or more, and in most cases the solution analyzed contained more formaldehyde than this. Furthermore, these results were obtained using 50–100% excess iodine and in the analysis of actual condensates a smaller excess was used. The thiosulfate equivalent of the iodine solution was checked frequently. The formaldehyde determination was also checked by the colorimetric method using Schiff's reagent by comparison with solutions of known formaldehyde content. Since the formaldehyde concentration was so small in most cases that several hours were generally required to develop the color, this method was not very accurate. On the other hand, it appears to be fairly specific, whereas a good many substances might conceivably interfere with the iodine method. In the majority of the runs, the iodine method gave higher results than the colorimetric

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(14) Bonnet, THIS JOURNAL, 27, 601 (1905).

which indicated the presence of some interfering substance. In one run (No. 84) in which the largest amount of product was obtained, the iodine method gave a definite precipitate which appeared to be iodoform. When correction was applied for the amount of iodoform obtained, the two methods checked quite well. In all the runs the two methods checked fairly well when one considers the very small amounts of formaldehyde present and this agreement is considered to be definite proof that formaldehyde was actually synthesized. In calculating equilibrium constants, the results of the colorimetric method were used.

Methanol was also determined by two methods, the oxidation method previously referred to and the colorimetric method developed by Smith and Branting from the methanol test of Wright.[15] If the latter method was carried out with great care, the two methods were found, by tests on known solutions, to agree within 10% even when only a few milligrams of methanol were present. In the actual analysis of condensates, the agreement was much better than this.

Consideration was given to several other substances which might, if present, interfere with the formaldehyde or methanol determination. Dimethyl ether has been shown by Dodge[16] to interfere with the colorimetric determination of methanol, and presumably it would also interfere with the oxidation method. Since no dehydrating catalysts were used in any of the final equilibrium runs, no dimethyl ether would be expected, but the following test was made to settle this point more definitely. Formaldehyde was hydrogenated at a temperature of 250° using the same catalyst that was used in the final equilibrium measurements. About 10 cc. of condensate was collected and, of this, 2 cc. was distilled into concentrated sulfuric acid, which was kept cold by a water-bath. Upon dilution of the acid and heating to 80°, no gas was set free. According to Erlenmeyer and Kriechbaumer[17] the solubility of dimethyl ether in cold sulfuric acid and its release on dilution and warming is characteristic (confirmed by McKee and Burke),[18] so the fact that no gas was given off was taken as evidence of the absence of dimethyl ether.

Methylal, which might possibly be formed, was found to interfere with the colorimetric determination of formaldehyde, but the color was crimson instead of the characteristic blue of formaldehyde. However, the interference with the iodine test was shown to be extremely small, so that a quantity of methylal sufficient to give a deep crimson color test would not interfere with the iodine method. From the fact that the Schiff's reagent color was always blue, and that the colorimetric and iodine methods for formaldehyde checked about as well as could be expected, it is concluded that methylal was not present in sufficient amount to affect either the formaldehyde or methanol determinations.

Catalysts.—In the study of the hydrogenation of formaldehyde, various catalysts were used in an attempt to obtain a clean-cut reaction. In the synthesis runs with hydrogen and carbon monoxide as starting materials only copper–zinc catalysts were used since previous work in this Laboratory had shown them to be the most active methanol catalysts. With the exception of the platinum and osmium catalysts, the procedures for their preparation were practically identical. All chemicals used were of the C. P. grade. The usual starting material was the metal or its oxide, which was dissolved in nitric acid and diluted to a concentration of 15 g. of metal per liter. Chromic nitrate, however, was prepared by the reduction of potassium dichromate with ethyl alcohol. The solutions were mixed to get the proper molal proportions and heated to the precipitation temperature. The precipitant was then added with stirring. The catalysts were then washed by decantation five or more times and filtered on a Buchner

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(15) Smith and Branting, THIS JOURNAL, 51, 129 (1929); Wright, *Ind. Eng. Chem.*, 15, 788 (1923).

(16) Dodge, *Ind. Eng. Chem.*, *Anal. Ed.*, 4, 23 (1932).

(17) Erlenmeyer and Kriechbaumer, *Ber.*, 7, 699 (1874).

(18) McKee and Burke, *Ind. Eng. Chem.*, 15, 788 (1923).

funnel. Some needed only to be dried at 105° and crushed to pass 8 mesh, the portion held on 16 mesh being used. Others were pressed in a hydraulic press to make a more dense cake and then dried and crushed. Some were so soft that they were formed into small pills in a pill machine usually with the aid of a few per cent. of graphite as binder. Table II gives the important facts concerning the catalysts used.

TABLE II

DATA FOR THE PREPARATION OF CATALYSTS

Catalyst	Molal composition[a]	Precipitant	Temp. of precipitation, °C.	Method of forming granules
1 and 1a	$CuZn_3$	Satd. Na_2CO_3	Room	Moist filter cake pressed
2 and 2a	Cu	30% NaOH	80	Dried and crushed without other treatment
3	Ni	30% Na_2CO_3	80	
4 and 4a	$Cu_{19}Zn$	30% Na_2CO_3	80	Pilled with 3% graphite
5	$Cu_{99}Ce$	30% Na_2CO_3	80	Pilled with 2% graphite
5a	$Cu_{99}Ce$	30% Na_2CO_3	80	Moist filter cake pressed
6	$Ni_{99}Ce$	30% Na_2CO_3	80	Dried and crushed without other treatment
7	$Cu_{19}Cr$	30% Na_2CO_3	80	Moist filter cake pressed
8 and 8a	Zn	30% Na_2CO_3	Room	Dried and crushed without other treatment
9	Os	Concd. NH_4OH	Room	Precipitated on acid-washed pumice
10	Pt	Alkaline formalin	Room	
11, 11a, 11b	$CuZn_3$	30% Na_2CO_3	Room	Moist filter cake pressed
11	$CuZn_3$	30% Na_2CO_3	Room	Pilled without binder
12	$CuZn_3$	30% Na_2CO_3	Room	Moist filter cake pressed
13	Zn_9Cr_{11}	Satd. Na_2CO_3	...	Dried and crushed without other treatment

[a] Determined from the weights of metals used.

Extreme care was taken with the preparation of No. 12 to ensure the absence of alkali in the finished catalyst. Besides using a deficiency of sodium carbonate, it was washed fifteen times by decantation.

The catalysts were reduced in place in the reactor, a mixture of two parts of hydrogen and one of carbon monoxide being used for all except the platinum and osmium ones, for which pure hydrogen was used. A slow stream of gas was maintained and the furnace allowed to heat up slowly to about 200° in the course of twenty-four hours, and then the temperature was held at this point for another twenty-four hours. The pure zinc catalyst was further activated at a temperature of 435° as it was found very inactive after the low temperature treatment.

Apparatus and Procedure.—The hydrogenation of formaldehyde and the reverse reaction were studied at atmospheric pressure and the formaldehyde synthesis reaction at three atmospheres. A few preliminary runs on formaldehyde synthesis at atmospheric pressure showed that a higher pressure was desirable in order to secure enough product to measure with even rough precision. Too high a pressure is undesirable because the ratio of methanol to formaldehyde in the product increases with pressure.

The investigation of formaldehyde hydrogenation necessitated a means of producing a mixture of hydrogen and formaldehyde vapor, preferably of definite and constant composition, and considerable work was done on this preliminary problem. The use of liquid formaldehyde, made by condensing the monomolecular vapor, according to the method of Trautz and Ufer was thought to offer a possible solution,[19] but it was found that the liquid so produced was not entirely dry even after several fractionations, so

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(19) Trautz and Ufer, *J. prakt. Chem.*, **113**, 105 (1926).

that when a portion had been evaporated the residue polymerized very rapidly. It was evident that this method would not enable one readily to obtain the relatively large amounts of formaldehyde vapor needed and hence it was abandoned. An attempt was made to dry the formaldehyde vapor by a number of desiccants such as phosphorus pentoxide, calcium chloride and anhydrone, but it was found that these reagents absorbed the formaldehyde without drying it, and in the case of phosphorus pentoxide the formaldehyde was actually decomposed. A number of experiments were made to determine whether the concentration of formaldehyde gas would be definite if hydrogen were passed over paraformaldehyde heated to a constant temperature. It was found that the concentration depended on the previous history of the paraformaldehyde as well as the temperature, since it decreased continually as the paraformaldehyde was evaporated. None of the other formaldehyde polymers appeared to offer any better solution to the problem. Inasmuch as this appeared to be the only practicable method, it was finally adopted, although it meant that a steady state was not attained and material balances could not be made.

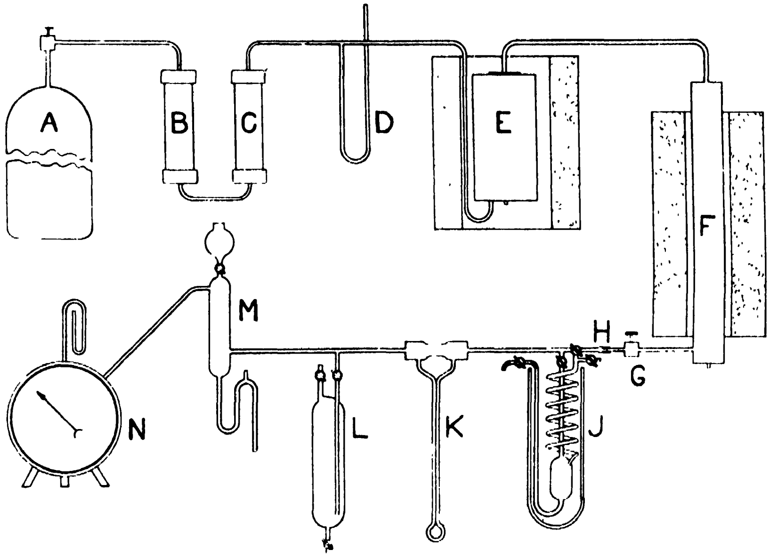

Fig. 1.—Arrangement of apparatus.

Essentially the same apparatus, with minor changes in details, was used for the study of both reactions. Referring to Fig. 1, the gas (hydrogen in the case of the hydrogenation and dehydrogenation reactions and a mixture of carbon monoxide and hydrogen for the synthesis reaction), stored in a steel cylinder A under a pressure of about 135 atm., was withdrawn through the usual diaphragm reducing valve, and passed through copper tubing into tube B (made of a 15 cm. length of standard $1^1/_4''$ (3.18 cm.) pipe, fitted with caps), containing a layer of silica gel 13 mm. deep to remove entrained oil, and a layer of Ascarite 12.5 cm. deep to remove carbon dioxide. Tube C, exactly similar to B, was filled with activated silica gel to remove any methanol or other condensable vapors from the gas and to dry it. D is a mercury manometer 2 meters high on which the total pressure of the system was measured. The formaldehyde saturator E, used only when hydrogenation of formaldehyde was under investigation, was made from 4" (10.2 cm.) brass tubing, 20.3 cm. long, with soldered brass heads. The top head had a 5.08 cm. hole for filling, closed by a brass cover, secured by studs and rendered gas-tight by an asbestos gasket. The saturator held about 700 g. of paraformaldehyde in the form of small pills. The temperature of the saturator was measured by a thermometer inserted in a well in the bottom. An electric furnace fitted over the saturator for heating to the desired temperature. The methanol saturator, used when the dehydrogenation reaction was studied, was interchangeable with that for formaldehyde, and was of similar construction but much smaller. For investigation of formaldehyde synthesis starting from carbon monoxide and hydrogen the saturators were omitted altogether and were replaced by a short piece of copper tubing. From E the gas passed through a tube, which was electrically heated to prevent condensation of the methanol or polymerization of the formaldehyde, to the reactor F, which is shown in detail in Fig. 2. This was constructed of 2″ (5.08 cm.) copper tubing, 25.4 cm. long, fitted with soldered brass heads, into which screwed brass plugs, aluminum gaskets being used for gas-tight connections. The catalyst bed was 15.2 cm. deep and was located in the exact center of an electric tube furnace. The ends of the reactor which projected beyond the furnace were well lagged with magnesia. This reactor had a capacity of 300 cc. of catalyst. A smaller reactor of similar design with a capacity of 30 cc. of catalyst and interchangeable with the larger one was used in some of the runs.

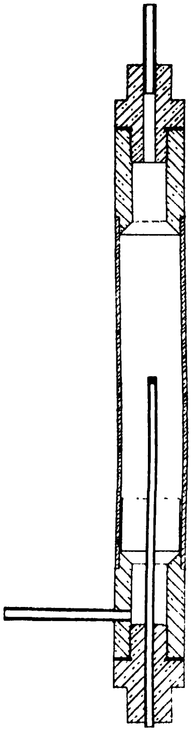
Fig. 2.—The catalyst reactor.

The temperature of the catalyst bed was measured by a calibrated thermocouple inserted in a well located in the center of the catalyst bed. A brass needle valve G was used to adjust the flow of gas to the desired value.

Up to G the apparatus was all metal, beyond it all glass, the connection being made by means of a copper–Pyrex seal at H. This was rather fragile, but otherwise gave satisfactory results. Two types of condensers were used, the type shown in the figure when a large amount of condensate was expected as in the case of hydrogenation and a plain "U" tube for smaller amounts as in the case of formaldehyde synthesis. The coil type could be used only with solid carbon dioxide as a refrigerant since the coils plugged if the temperature were low enough to freeze the methanol. The "U" type was used with liquid air as a cooling medium to ensure complete condensation of the very small amounts of formaldehyde and methanol produced. It also had the advantage of being small enough so that it could be weighed on an analytical balance, thus obtaining the weight of condensate as a check on the analytical results. Constant flow of gas was indicated by means of the flowmeter K. A gas sample was taken as nearly continuously as possible, with the sampler L, which was designed to give a constant rate of sampling. The gas was finally saturated with water in the saturator M, and the total volume determined by the calibrated wet-test meter N.

In the experiments on the hydrogenation of formaldehyde the temperature of the catalyst was maintained manually at the desired figure. Since the reaction was strongly exothermic in most cases, and conditions not closely reproducible, it was very difficult to maintain any particular temperature. The synthesis runs starting from carbon monoxide and hydrogen were much longer, varying from 5 to 122 hours in length, and automatic temperature regulation was necessary. This was obtained by means of a relatively simple photo-electric type of controller which has been described in detail elsewhere.[20] With this apparatus, the temperature of the furnace could be controlled within 1.0° at any desired temperature regardless of fluctuations of line voltage. (In several

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(20) Newton and Furnas, *Chem. Met. Eng.*, **39**, 455 (1932).

runs the maximum variation was only ±0.1°.) A Leeds and Northrup recording potentiometer was used to check the temperature continuously while the operator was away.

The reducing valve held the pressure very constant, the variation in absolute pressure being largely due to changes in the barometer. In the runs at 3 atm. the uncertainty in the pressure was probably not more than ±0.01 atm.

Naturally the exact technique of operation varied according to the reaction being studied. In general the reactor was allowed to come up to temperature before the gas stream was started. If the paraformaldehyde saturator was being used, it was also allowed to come up to operating temperature before the gas was started. The methanol saturator was not heated, since a high enough concentration of methanol could be obtained at room temperature. During this "warm-up" period the gases were by-passed around the cold condenser to the flowmeter so that the rate of flow of gas could be set at the desired figure. Before a run the condenser was always washed out with pure methanol and dried by a stream of air sucked through it by means of a water jet pump. This was usually continued for about half an hour to ensure that no methanol was left in the condenser. When conditions had become constant, and had remained so for about fifteen minutes, the run was started by immersing the condenser in the cooling bath and cutting out the by-pass. The gas sampler was not started until a few minutes later in order to allow time for the air in the condenser to be swept out. Readings were taken at regular intervals, their frequency depending on the length of the run. It was found desirable to test the apparatus for leaks immediately before and after each run.

When liquid air was used as a cooling medium, any carbon dioxide and water formed in the reaction condensed as a solid in the upper part of the condenser and would cause stoppage of the flow if allowed to accumulate. Hence it was necessary in the longer runs to melt it out about twice a day. This was done by warming the condenser with the fingers at the point where the plug had formed and, in general, this dropped to the bottom of the "U" tube where it did no harm.

Since only very small amounts of formaldehyde and methanol were collected in the synthesis runs, it was necessary to make a blank run to be certain that the products determined actually came from reaction and not from some other source. A run of thirty-eight hours' duration was made using nitrogen gas, at a temperature of 250° and pressure of about 2 atm. and with the identical catalyst used in the final synthesis runs. No product was visible in the condenser, and no test for either methanol or formaldehyde was obtained by either of the two methods of analysis, on the liquid obtained by rinsing out the condenser with a small amount of water.

Experimental Results

Hydrogenation of Formaldehyde.—Forty-seven runs were made in the study of this reaction over the temperature range 117–237°, the majority being in the direction of hydrogenation. They are not closely reproducible for several reasons, one being the difficulty in maintaining steady conditions already mentioned, another the fact that the activity of the catalysts changes with use and finally the fact that the reaction is not clean and slight changes in conditions appear to exert considerable influence on the extent of side reactions in relation to the main reaction. The space velocities were higher than would normally be used for a close approach to equilibrium but this reaction appears to be quite rapid and nothing was gained by going to lower rates of flow because of the rapid increase in extent of side reactions.

Nine of these runs have been selected as most suitable for the calculation of an equilibrium constant. The basis for selection was mainly the fact that these runs are closely grouped about a given temperature. Due to the uncertainty of the thermal data, the effect of temperature on the equilibrium constant cannot be calculated with any degree of assurance. The results calculated from the observed data for these nine runs are presented in Table III.

TABLE III

EXPERIMENTAL RESULTS ON THE HYDROGENATION OF FORMALDEHYDE

				Distribution of carbon among products						
Run[a]	Temp., °C.	Catalyst	Space velocity[b]	% as CO_2	% as CH_4	% as CO	% as HCOH	% as CH_3OH	% as methyl formate	Kp[c]
28	200	4a	85	4.3	0.6	19.1	0.0043	73.0	3.0	2400
34^D	192	4b	180	1.8	.9	4.7	.25	86.8	5.6	404
35^D	189	4b	225	1.1	.4	4.7	.078	87.5	6.5	1740
36^D	191	4b	225	0.0	.0	3.2	.29	93.7	2 8	414
37	201	4b	450	1.9	.1	7.0	.15	39.9	52.8	2400
38	201	4b	425	0.8	.1	3.2	.14	29.9	68.9	3000
39	201	4b	450	0.7	.0	2.8	.26	24.0	72.3	3450
40^D	200	1a	380	5.9	1.8	23.9	.065	68.3	0.0	1950
42^D	203	8a	370	1.6	0.7	3.5	.048	94.4	.0	3080

[a] D signifies that equilibrium was approached from the dehydrogenation side.

[b] Liters of exit gas (at standard conditions) per liter of catalyst volume per hour.

[c] $Kp = Px_{\text{MeOH}}/Px_{\text{HCOH}}Px_{\text{H}_2}$, where P is the total pressure and x is mole fraction.

The calculated values of Kp agree remarkably well when one considers the extent of the side reactions that occurred in some cases. That an approximation to the equilibrium state was reached is indicated by the agreement between hydrogenation and dehydrogenation runs. Averaging the temperature and Kp values, one obtains the result $t = 197°$, $Kp = 2090$.

TABLE IV

EXPERIMENTAL RESULTS FOR FORMALDEHYDE SYNTHESIS

					Mg. of formaldehyde		
Run[a]	Temp., °C.	Space velocity[b]	Press., atm.	Duration of run, hrs.	Iodine method	Colorimetric	$Kp \times 10^5$
50	243	11.3	3.00	25.0	0.27	0.50	0.88
51	243	17.9	2.99	46.0	2.12	1.90	2.01
52	243	7.3	3.05	45.3	1.33	0.50	0.85
54	247	2.6	3.11	59.3	0.90	..	2.40
55	243	15.0	3.06	16.0	1.00	1.25	2.30
56	243	10.9	3.06	34.8	0.96	0.62	0.64
77	250	7.4	3.01	45.8	3.46	1.50	1.80
79	250	10.4	3.01	17.5	1.36	0.94	2.15
80^D	250	22.2	3.00	7.5	1.14	0.88	2.05
81^D	250	12.3	3.00	17.7	1.56	0.78	1.87
82	225	9.2	3.01	7.0	..	0.68	3.81
83^D	225	13.1	3.00	13.1	..	0.65	3.52
84	225	18.8	3.01	55.0	5.90	5.00	2.36
85^D	250	25.0	2.98	5.2	0.80	0.80	2.00

[a] D indicates methanol decomposition run. [b] Same units as in Table III.

Synthesis of Formaldehyde.—These runs were all made with the copper–zinc catalysts (Nos. 1, 11 and 12) at a pressure of 3 atmospheres absolute. The results are summarized in Table IV.

Since the effect of temperature on this equilibrium constant is small, the values for the first ten runs and that for run 85 have been averaged to give a value of $Kp = 1.72 \times 10^{-5}$ at 247°. For 225° the value of run No. 84 has been chosen as being the most reliable since the amount of formaldehyde produced was much greater than in any of the other runs. The fact that decomposition runs give constants of the same order of magnitude as those for synthesis is good evidence that the values cannot be far from equilibrium ones.

Discussion of Results

The following conclusions have been drawn from a study of all the runs on hydrogenation of formaldehyde.

1. Formaldehyde is readily and practically completely hydrogenated at temperatures from 120 to 200° over all of the catalysts except the osmium, platinum, and pure zinc catalysts which were quite inactive.

2. Nickel catalysts promote the decomposition of formaldehyde into carbon monoxide and hydrogen more than the copper catalysts. With the nickel catalysts, carbon monoxide was one of the major products even at as low a temperature as 120°, whereas with the copper catalysts, this was not the case until the temperature exceeded 150°, or usually higher.

3. In some of the runs, particularly with copper catalysts, relatively large amounts of methyl formate were produced. In one case nearly 80% of the carbon appeared in this form in the products.

4. The composition of the products from a given type of catalyst appears to be greatly influenced by slight variations in its structure caused either by variations in the method of preparation or changes that occur as the catalyst is used. Thus a given filling of catalyst No. 4 was used in three consecutive runs under as nearly identical conditions as could be maintained. In the first run, only 4% of the carbon in the products was in the form of methyl formate and 90% as methanol, whereas in the third run of the series, 78% appeared as methyl formate and 20% as methanol.

In order to deal with the equilibria over a range of temperatures, it is assumed that the variation of Kp with temperature may be represented by the equation

$$\log_{10} Kp = (-\Delta H/4.577) + C$$

Using the best available thermal data and evaluating C from the equilibrium constants given above, there are obtained the equations

$$\log_{10} Kp_1 = (374/T) - 5.431 \text{ (formaldehyde synthesis)} \quad (1)$$

$$\log_{10} Kp_2 = (4600/T) - 6.470 \text{ (hydrogenation of formaldehyde)} \quad (2)$$

A further proof that the measured equilibrium constants are of the correct order of magnitude may be had by calculating Kp_1 and Kp_2 for 250° by the above equations and comparing their product with the published values for the methanol equilibrium. $Kp_1 \times Kp_2$ at 250° $= 4 \times 10^{-3}$ and the values for the constant of the methanol synthesis equilibrium vary over the range from 1×10^{-3} to 5×10^{-3}.

To show what the possibilities are for the synthesis of formaldehyde from carbon monoxide and hydrogen and for the production of formaldehyde by dehydrogenation of methanol, results calculated from equations (1) and (2) are presented in Table V.

TABLE V

CALCULATED CONVERSIONS TO FORMALDEHYDE

Temp., °C.	Press., atm.	Kp_1	Kp_2	Percentage conversion to formaldehyde	
200	1	2.30×10^{-5}	1800	2.4	(Methanol dehydrogenation)
200	300	2.30×10^{-5}	1800	0.35	(Formaldehyde synthesis)
250	1	1.92×10^{-5}	210	6.9	(Methanol dehydrogenation)
350	1	1.48×10^{-5}	8.3	32.8	(Methanol dehydrogenation)
450	1	1.22×10^{-5}	0.8	74.5	(Methanol dehydrogenation)

The result for formaldehyde synthesis is based on the assumption that $CO + H_2 = HCOH$ is the only reaction taking place. As a matter of fact it has already been shown that formaldehyde is very easily hydrogenated and one can safely say that any catalyst that will promote the hydrogenation of carbon monoxide will certainly promote the further hydrogenation to methanol. The maximum possible yield of formaldehyde assuming that equilibrium is reached with respect to both reactions is readily calculated and is considerably less than the yield from the first step alone. For the specific case chosen, the conversion would be extremely small because of the high conversion to methanol that is possible. At 350° and 300 atm. about 0.10% would be the conversion to formaldehyde. We may, therefore, conclude that the direct synthesis of formaldehyde from carbon monoxide and hydrogen is not feasible at any reasonable temperature or pressure. Our results also show that none of the previous investigations of formaldehyde synthesis at atmospheric pressure would have yielded enough formaldehyde to give a positive test, confirming the conclusions of Marshall and Stedman.

It is also evident that methanol cannot be appreciably dehydrogenated to formaldehyde at temperatures of 200° and below, and to secure good yields temperatures of over 400° are necessary.

Summary

The position of equilibrium for the reactions $H_2 + CO \rightleftharpoons HCOH$ (1) and $H_2 + HCOH \rightleftharpoons CH_3OH$ (2), has been investigated at temperatures from 200–250° and at 1 to 3 atmospheres pressure. The best values for Kp are 1.72×10^{-5} at 247° for reaction (1) and 2090 at 197° for reaction (2). The following equations for the variation of Kp with temperature are

suggested: $\log_{10} Kp_1 = (374/T) - 5.431$ and $\log_{10} Kp_2 = (4600/T) - 6.470$. The significance of these results in the practical synthesis of formaldehyde is discussed.

NEW HAVEN, CONNECTICUT

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Thermodynamic Properties of Trifluorotrichloroethane and Difluorotetrachloroethane

BY FRANK HOVORKA AND FRANCIS E. GEIGER

In the study of the fluorination of hexachloroethane at high temperatures and pressures, Booth, Mong and Burchfield[1] obtained, among others, two liquid compounds, $C_2F_2Cl_4$ and $C_2F_3Cl_3$. A few of the more common physical constants were determined by them, but these only at one temperature. In view of the possible industrial importance of these liquids, it was considered quite desirable to determine accurately their physical constants over a wide range of temperature.

Purification of Materials.—The materials were furnished through the kindness of Dr. Booth of this Laboratory. The $C_2F_2Cl_4$ was refluxed over barium oxide to remove any water which might be present. Then it was fractionally distilled, using a special high fractionating column until a boiling point constant to 0.05° was obtained. Crystallization of this liquid did not affect the boiling point of the liquid. The $C_2F_3Cl_3$ on account of its low boiling point was distilled directly from barium oxide and condensed with carbon dioxide snow to avoid any excessive loss by evaporation. It was then fractionally distilled until a boiling point constant to 0.04° was obtained.

Apparatus and Procedure.—The various physical constants were determined by practically the same method as that described by Hovorka, Lankelma and Naujoks.[2]

Discussion of Results.—In the case of each liquid the boiling point was obtained by extrapolation of the vapor pressure–temperature curve. The heat of vaporization was calculated from the slope of a line obtained by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Sugden's parachor and the critical temperature were obtained by the usual methods. All of these are summarized in Table I.

The freezing point of $C_2F_2Cl_4$ was found to be 28.1°. Its Eötvös constant was 2.34. All the other properties as shown in the Table exhibited the usual variation of a normal liquid.

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(1) Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932).

(2) Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933).

TABLE I

PHYSICAL PROPERTIES OF COMPOUNDS

DIFLUOROTETRACHLOROETHANE

Molal heat of vaporiz., 8350 cal.; crit. temp., 278.0°C.; Sugden's parachor, 271.9

T, °C.	Abs. density	Visc. $\times 10^3$	Surf. tens.	Index of refr.	V. p., mm.
28.1	1.6396[a]	12.47[a]	22.98[a]	1.4119[a]	65.8
30.0	1.6358	12.08	22.73	1.4109	72.2
40.0	1.6157	10.36	21.56	1.4069	108.6
50.0	1.5959	9.08	20.44	1.4015	164.3
60.0	1.5754	7.96	19.38	1.3960	243.6
70.0	1.5552	7.13	18.36	1.3900	357.1
80.0	1.5356	6.29	16.93	1.3840	509.3
90.0	1.5146	5.66			

T, °C.	10.0	20.0	85.0	91.0	91.50 ± 0.05
V. p., mm.	28.9	45.8	604.9	744.3	760.0[a]

TRIFLUOROTRICHLOROETHANE

Molal heat of vaporiz., 7010 cal.; crit. temp., 187.6°C.; Sugden's parachor, 244.2

T, °C.	Abs. density	Visc. $\times 10^3$	Surf. tens.	Index of refr.	V. p., mm.
0.0	1.6195	9.25	19.85	1.3697	109.3
10.0	1.5971	8.05	18.96	1.3642	177.3
20.0	1.5760	7.11	17.75	1.3590	272.5
30.0	1.5531	6.27	16.56	1.3539	406.4
40.0	1.5278	5.59	15.30	1.3480	588.2
46.0					727.4
47.25 ±).04					760.0[a]

[a] Value obtained by extrapolation.

In the case of $C_2F_3Cl_3$ the physical properties (Table I) showed a fairly uniform variation, with the exception of surface tension. Here the surface energy variation with temperature did not produce a straight line. The value of Eötvös constant for this liquid is 2.59 near its boiling point, while at 0° it is 1.69. This would indicate that the liquid is probably associated. That may not be surprising if one considers the unsymmetrical arrangement of fluorine and chlorine atoms in this compound as compared with $C_2F_2Cl_4$ where we have a well-balanced molecule and apparently no association.

In the case of both of these liquids the calculated value for the parachor is higher than the value calculated from experimental results. It is probable that the theoretical value of the parachor constant of fluorine is too high because the same variation was noticed for all the other fluorine compounds thus far studied.

The vapor pressure variation with temperature of $C_2F_2Cl_4$ may be expressed by the equation

$$\log P = (-764.783/T) + 7.4446 \log T - 14.0934$$

and for $C_2F_3Cl_3$

$$\log P = (-2030.38/T) - 3.69666 \log T + 18.4810$$

where pressure is expressed in millimeters of mercury, and T is absolute temperature.

Summary

The following physical properties for $C_2F_2Cl_4$ and $C_2F_3Cl_3$ have been determined over a wide temperature range: density, index of refraction, surface tension, vapor pressure and viscosity.

Critical temperatures, molal heat of vaporization, parachor and vapor pressure–temperature equation have been calculated for each liquid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ROCHESTER]

The Decomposition of Formic Acid by Sulfuric Acid

BY ROBERT E. DERIGHT

Introduction

A study of the decomposition of formic acid by sulfuric acid has been reported by Schierz,[1] who also cites early workers in this field. Schierz, and later Schierz and Ward,[2] determined the velocity of decomposition in sulfuric acid solutions as concentrated as 96.69%. The results obtained can be accounted for on the basis of Taylor's theory of negative catalysis.[3]

Since the decomposition of several organic acids by sulfuric acid, when small amounts are dropped into large amounts of sulfuric acid, follows the unimolecular law it was thought that some light might be cast on the mechanism of the reaction if the conditions were reversed. In this case the concentration of formic acid would not change; hence, the true order of the reaction might be determined.

The effect of water in smaller concentration and the effect of sulfur trioxide were also thought worthy of investigation.

Experimental Part

Preparation and Purification of Materials.—The 85% formic acid was concentrated by the method described by Schierz[1] and the last traces of water removed by the method described by Coolidge.[4] The formic acid thus obtained was run from a glass stoppered storage bottle through an all glass siphoning system to a micro-buret, air being admitted through a drying train.

Four sulfuric acid solutions corresponding to 94.74, 100.16, 100.08 and 106.5% were prepared. The first solution was the ordinary C. P. reagent, the second and third were prepared by mixing C. P. fuming sulfuric acid and the ordinary reagent, and the fourth solution consisted of C. P. 30% fuming sulfuric acid. The 94.74 and the 106.5% acids were analyzed by precipitation as barium sulfate, due precautions being taken to prevent absorption of water and loss of sulfur trioxide. The 100.16 and 100.08% solutions were found by preliminary experiment to be slightly fuming, they melted at 9.99 and 10.25°, respectively, so that their concentration could be determined from the data

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(1) Schierz, THIS JOURNAL, **45**, 447 (1923).

(2) Schierz and Ward, *ibid.*, **50**, 3240 (1928).

(3) Wiig, *ibid.*, **52**, 4742 (1930).

(4) Coolidge, *ibid.*, **50**, 2166 (1928).

of Hantzsch.[5] Velocity coefficients of the decomposition of oxalic and citric acids in mixtures of these acids were in close agreement with those of Wiig,[6] a further proof of the analysis. The acids were run to burets in the same manner as the formic acid.

Apparatus and Method of Procedure.—The velocity of decomposition of the formic acid was observed by measuring the carbon monoxide evolved over certain periods of time. The reactions were carried out in 50-cc. round-bottomed flasks, of special design, supported in a thermostat by an agitator. Two types of agitators were used, one a pendulum type described by Bent[7] and the second of the type described by Walton.[8] The agitators were so arranged that the flasks were completely immersed in a thermostat regulated to ±0.01°. Supersaturation of the solution by carbon monoxide was prevented by the addition of small pieces of Pyrex glass rods, and by indentations in the bottoms of the flasks. The carbon monoxide formed was conducted by capillary tubing to water-jacketed burets held at the same temperature as the thermostat.

In order to obtain sulfuric acid of the desired concentration, calculated amounts (total 25 cc.) of the stock solutions were run into the reaction flask, stoppered to the buret, the pressure being slightly diminished to permit flow of the acid. The sulfuric acid or formic acid was dropped into the reaction mixture when it had come to the temperature of the thermostat.

Experimental Results

I. Formic Acid as Solvent

In the investigations dealing with decomposition of formic acid by sulfuric acid, a small quantity of the acid was dropped into proportionately large quantities of sulfuric acid. The decompositions followed the unimolecular law. These data have not shown whether the reaction is truly unimolecular, *i. e.*, decomposition of an intermediate compound between the organic acid and sulfuric acid, or only apparently so, due to the negligible change in the sulfuric acid concentration. Since formic acid is the only organic acid studied which is liquid at room temperature, it lent itself as a medium into which small amounts of sulfuric acid might be dropped.

Samples of 0.5 to 1.0 cc. of 94.74 and 100.18% sulfuric acid were dropped into 10-cc. portions of formic acid. Temperatures from 25 to 50° were employed. In every case when the capsule dropped into the formic acid, 25 to 50 cc. of gas was suddenly evolved. This sudden evolution of gas slowed down abruptly, continuing at a steadily diminishing rate. Continuous experiments were carried out over a period of ten days, at the end of which time gas was still being evolved. The rate did not correspond to either the unimolecular or bimolecular law, but seemed to fall off as water was formed in the reaction. The volume of carbon monoxide evolved over long periods of time corresponded to an amount of water sufficient to hydrate each molecule of sulfuric acid with two to three molecules (of water).

If the decomposition is due to the disintegration of an intermediate compound between the sulfuric acid and the organic acid, the sulfuric acid must be regenerated after decomposition of the compound. The inhibitory

(5) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908).

(6) Wiig, THIS JOURNAL, **52**, 4729, 4737 (1930).

(7) Bent, *Ind. Eng. Chem., Anal. Ed.*, **2**, 106 (1930).

(8) Walton, *Z. physik. Chem.*, **47**, 185 (1904).

effect of the water must be due to hydration of the sulfuric acid or intermediate compound, as the large quantity of formic acid present prevents any effect by hydration of it.

II. Sulfuric Acid as Solvent

A. The Effect of Water on the Reaction.—Schierz[1] and later Schierz and Ward[2] have shown the decomposition of formic acid by sulfuric acid to be a unimolecular reaction, and hence the equation $K = 2.303/t \log a/(a - x)$ applies. The velocity constants are independent of the speed of shaking, if rotary shaking of the type described by Walton[8] is employed. The velocity of the reaction may be dependent on the speed of shaking if a pendulum type shaker is used. Several shaking speeds were employed but concordant results with formic acid could not be obtained nor could the measurements of the decomposition of citric acid be repeated above a velocity constant of 200×10^3 with the latter shaking device.

A typical experiment is shown below. It is to be noted that at this concentration the velocity constants do not fall off rapidly. At higher concentrations of sulfuric acid these constants fall off considerably. At a concentration of 100% sulfuric acid the constants fall off as much as 35%, due to the strong inhibitory effect of water. This is in agreement with the results of Lichty[9] and of Wiig[6] on oxalic acid.

TYPICAL EXPERIMENT

Temp., 15 °C. Molality of H_2O, 0.28 (99.5% H_2SO_4). $a = 33.5$

t	0.5	1	1.5	2	3
x	9.8	16.7	21.5	24.7	28.4
$a - x$	23.7	16.8	12.0	8.8	5.1
$k \times 10^3$	691	679	684	668	626

In Table I is given the velocity constant corresponding to various percentages of water present. Each value corresponds to the average velocity constant at 50% decomposition in from three to ten experiments.

TABLE I

THE EFFECT OF WATER ON THE REACTION RATE AT 15°

Water, %	3.98	2.99	1.97	1.49	0.83	0.50	0.23	0.10	0.00
Molality of water	2.30	1.71	1.12	0.84	.47	.28	.09	.06	.00
$K \times 10^3$	50.4	82.0	156.6	222.0	491	677	1686	2677	4126

Figure 1 shows the data graphically. These data show that the effect of water is to inhibit the decomposition, the relative effect decreasing with increasing amounts of water. Similar results have been obtained for the other organic acids studied, as cited by Wiig.[6]

B. The Effect of Sulfur Trioxide on the Reaction.—Due to the marked increase in the velocity of decomposition with decreased concentration of water, it was possible to make a quantitative determination of the

(9) Lichty, *J. Phys. Chem.*, **11**, 225 (1907).

velocity at only one concentration above 100% H_2SO_4 at 15° and 100.08% H_2SO_4 (0.36% SO_3), $K = 4888 \times 10^{-3}$. This value shows how rapidly the velocity constants increase.

The temperature of the thermostat was then lowered to 5°. At this temperature it was impossible to determine velocity constants at concentrations of less than 100.2% H_2SO_4 because of freezing. Approximate velocity constants were determined for 0.89 to 3.31% SO_3 (100.2 to 100.7% H_2SO_4). Over this range the very rapid velocity constants increased only slightly, indicating that the effect of SO_3 was diminishing. Qualitative measurements at 4.44% SO_3 (101.0% H_2SO_4) and 28.88% SO_3 (106.5% H_2SO_4) gave immeasurably high velocity constants, but of the same order of magnitude.

These qualitative relationships show the effect of sulfur trioxide on the decomposition of formic acid to be concordant with that obtained for oxalic, citric and malic acids. Discussion of these results will be postponed until further work, now in progress, is completed.

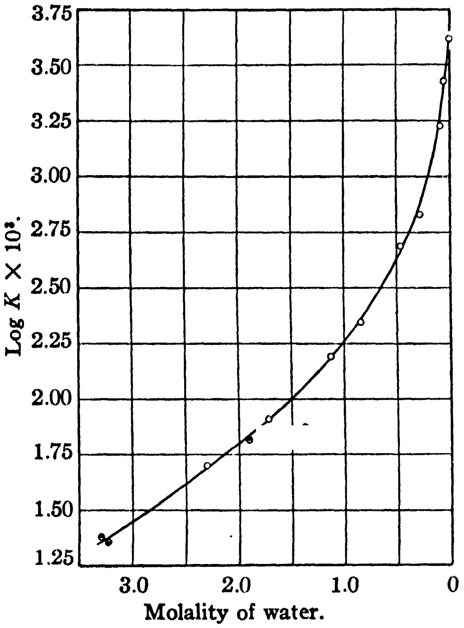

Fig. 1.—○, Author; ⊖, Schierz; ●, Schierz and Ward.

The author wishes to express his sincere appreciation to Dr. Edwin O. Wiig, under whose direction this work has been done and who has lent much material help in the completion of it.

Summary

1. The decomposition of formic acid by small quantities of sulfuric acid proceeds indefinitely, the rate of decomposition progressively diminishing as water is formed in the reaction.

2. Measurements of the decomposition of formic acid by sulfuric have been extended to a concentration of 100% sulfuric acid.

3. Qualitative determination of the effect of sulfur trioxide is concordant with that obtained in the case of oxalic, citric and malic acids.

4. A pendulum type of shaker does not give concordant results for rapid reactions.

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The Rate of Oxidation of Hydrogen Peroxide by Chlorine in the Presence of Hydrochloric Acid

BY BENJAMIN MAKOWER AND WILLIAM C. BRAY

The rapid reaction between hydrogen peroxide and chlorine

$$H_2O_2 + Cl_2 = O_2 + 2H^+ + 2Cl^- \tag{1}$$

has been shown by Livingston and Bray[1] to be involved in the catalytic decomposition of hydrogen peroxide in the presence of hydrochloric acid and chlorine. By analogy with the bromine–bromide system,[2] the mechanism of Reaction 1 was interpreted in terms of a single rate-determining reaction

$$H_2O_2 + HOCl \longrightarrow O_2 + H^+ + Cl^- + H_2O \tag{2}$$

and a rapid reversible equilibrium, the hydrolysis of chlorine

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{3}$$

The kinetic investigation presented in this paper was undertaken to test the predicted rate law

$$-d(H_2O_2)/dt = \kappa_2(H_2O_2)(HOCl) = k_2(H_2O_2)(Cl_2)/(H^+)(Cl^-) \tag{4}$$

where

$$k_2 = \kappa_2 K' \quad \text{and} \quad K' = (HOCl)(H^+)(Cl^-)/(Cl_2) \tag{5}$$

The corresponding rate law has already been verified in the case of the closely related peroxide–bromine reaction[3] and the methods described below are similar to those used in the earlier investigation.

Methods

The rate of Reaction 1 was measured by following iodimetrically the decrease in total oxidizing power. The reaction was "quenched" by rapidly mixing a known volume of the reaction mixture with a solution which contained sufficient amounts of potassium iodide and $Na_2HPO_4 \cdot 12H_2O$ to have 2% potassium iodide and not over 0.2 M H^+ in the final solution. The resulting mixture was set aside in the dark for about one hour to allow time for the relatively slow reduction of hydrogen peroxide, and the liberated iodine was then titrated with thiosulfate. The low concentration of acid and the protection from light were necessary in order to minimize the oxygen error due to the reaction between O_2, I^- and H^+ (ref. 3, p. 1658).

At concentrations of hydrochloric acid between 0.35 and 2 N, the reaction was so rapid that it was necessary to resort to a special method of starting and quenching the reaction, namely, the *flow method;* at higher concentrations of the acid, when the rate was sufficiently low, the reaction mixtures

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(1) Livingston and Bray, THIS JOURNAL, **47**, 2069 (1925).

(2) Bray and Livingston, *ibid.*, **45**, 1251 (1923).

(3) Bray and Livingston, *ibid.*, **50**, 1654 (1928).

were analyzed by extracting samples at various time intervals. This was called the *sampling method.*

The application of the *flow method* to the study of high reaction velocities in solutions was first made by Hartridge and Roughton[4] and later by Roughton,[5] Bray and Livingston,[3] Saal,[6] Schmid[7] and La Mer and Read.[8] The principle of the method and the type of apparatus used in the present work are given in detail by Bray and Livingston.[3] Only certain modifications and improvements of the apparatus, Fig. 1, some of which are due to personal suggestions of Dr. Roughton, will be discussed here.

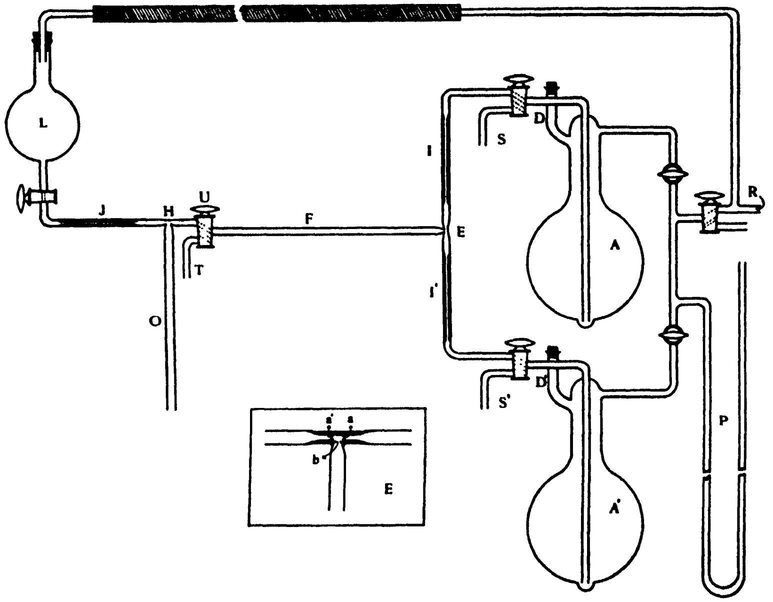

Fig. 1.—The flow apparatus.

On the application of pressure the component solutions of known concentrations (one containing hydrogen peroxide and the other chlorine) were forced to flow from A and A′ through I, I′, and to mix in a T-shaped mixing chamber E in less than one-fiftieth of a second. The reaction mixture then moved along the tube F, mixed with the "quenching solution" from L in another slightly larger mixing chamber H, and was finally collected in a two-liter volumetric flask placed beneath the tube O. An aliquot portion of this solution was later analyzed for the iodine content to determine the extent to which the reaction had proceeded. The time of the reaction, τ, was that necessary for the reaction mixture to travel from the first to the second mixing chamber. It was calculated from the expression $\tau = ut/V$, where u is the known volume of the reaction tube between E and H, and V is the volume of the solution delivered through tube O

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(4) Hartridge and Roughton, (a) *Proc. Roy. Soc.* (London), **A104**, 376 (1932); (b) *Proc. Camb. Phil. Soc.*, **22**, 426 (1924), and **23**, 450 (1926).

(5) F. J. W. Roughton, *Proc. Roy. Soc.* (London), **A126**, 439 (1930).

(6) R. N. J. Saal, *Rec. trav. chim.*, **47**, 73 (1926).

(7) H. Schmid, *Z. physik. Chem.*, **A141**, 41 (1929).

(8) La Mer and Read, THIS JOURNAL, **52**, 3098 (1930).

in the time t. The mixing chamber E (also shown in the inset E) was of a simple type originated by Hartridge and Roughton (Ref. 4a, p. 378). It consisted of a T-tube of low resistance to flow, and was made of 7-mm. tubing which was reduced at "a" to 2 mm. and at "b" to 3 mm. The cross sectional area at "b" was approximately twice that at "a." The Y-shaped mixing chamber, previously used by Bray and Livingston,[8] had determined the rate of flow because of its very high resistance. The rate of flow in the present apparatus was controlled more conveniently by means of capillary tubing in the system. I and I′ were 1-mm. capillaries 7 cm. long; J was a 2-mm. capillary 23 cm. long, so chosen that a volume of the reacting solution mixed with an approximately equal volume of the quenching solution from the liter flask L.

Details of operation and principles underlying the construction of a flow apparatus are given by Makower.[9]

The sampling method procedure was as follows. A measured volume of the reaction mixture containing all reagents with the exception of hydrogen peroxide was placed in a 500-cc. glass-stoppered flask and allowed to attain temperature equilibrium in a thermostat. Two 20-cc. samples of this mixture were withdrawn and analyzed iodimetrically for chlorine. The run was then started by adding 3 cc. of stock hydrogen peroxide solution with a pipet. After replacing the stopper, the flask was shaken vigorously by hand outside the thermostat; the time of the shaking was taken as the initial time for the reaction. At intervals, 20-cc. samples of the reaction mixture were pipetted into 125-cc. glass-stoppered flasks containing the quenching solution and were analyzed by the method described above. The time at which the pipet was half empty was taken as the quenching time. At the end of the run a portion of the remaining reaction mixture was analyzed for the concentration of acid by titration with a standardized solution of sodium hydroxide. If any chlorine was still present it interfered with the titration by destroying the indicator. Excess of hydrogen peroxide was therefore added to remove the chlorine and the sample was then titrated using methyl red as the indicator. The error due to formation of more hydrogen ion by this process is negligible. Incidentally, methyl red may be used to detect very small traces of chlorine in solution.

The concentrations of any other reagents used in the preparation of the reaction mixture were calculated from known weights or concentrations of these substances initially added and from the final volume of the reaction mixture. The specific gravities of concentrated reaction mixtures were also determined.

In the calculation of specific rates, since the concentrations of H^+ and Cl^- ions were relatively high and remained virtually constant during any one experiment, Equation 4 could be used in the form

$$-\mathrm{d}(H_2O_2)/\mathrm{d}t = k(H_2O_2)(\Sigma Cl_2) = k(A - x)(B - x)\text{[10]} \qquad (6)$$

where $(\Sigma Cl_2) = (Cl_2) + (Cl_3^-)$ and $k_2 = k(H^+)(Cl^-)[(\Sigma Cl_2)/(Cl_2)]$. A and B, are, respectively, the initial (H_2O_2) and (ΣCl_2). x is the decrease in (ΣCl_2) or (H_2O_2) in the time t minutes, and is calculated from the relation, $x = [(A + B) - (A + B - 2x)]/2$.

In the flow method experiments, k was calculated from the integrated expression for a second order reaction

$$k = \frac{2.303}{(A - B)t} \log \frac{(A - x)\,(B)}{(B - x)\,(A)}$$

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(9) Makower, Ph.D. Thesis, May, 1932, University of California Library. This thesis may also be consulted for details omitted in the present paper.

(10) The symbol "( )" will be used to indicate "concentration of" in moles per liter.

while in the experiments done by the sampling method the calculations were carried out by the usual graphical method of plotting log $[(A - x)/(B - x)]$ against t, and multiplying the slope of the line by $2.303/(A - B)$.

The experimental results were expressed in terms of the specific rate k_2' which is related to k and k_2 by the equations

$$k_2' = k(\mathrm{H}^+)(\mathrm{Cl}^-) \quad \text{and} \quad k_2 = k_2'(\Sigma\mathrm{Cl}_2)/(\mathrm{Cl}_2) \tag{7}$$

Experimental Results at 25°

The Effect of Varying (HCl).—The results of the experiments at 25° in the presence of hydrochloric acid are summarized in Table I according to increasing concentration of the acid.

TABLE I

EXPERIMENTAL RESULTS IN SOLUTIONS OF HCl AT 25°

Run	$(H_2O_2)\ 10^3$	$(\Sigma Cl_2)\ 10^3$	(HCl)	$x(10^3)$	$\tau\ (10^2)$, min.	$k_2'(10^{-3})$
36	7.27	1.64	0.357	1.13	1.84	1.23
37	7.27	1.64	.357	1.26	2.32	1.28
47	7.11	10.10	.368	4.72	1.63	1.29
59	16.59	5.78	.369	5.16	1.74	1.35
60	16.59	5.78	.369	5.14	1.73	1.33
65	18.29	6.11	.378	5.55	1.68	1.42
66	18.29	6.11	.378	5.52	1.70	1.36
45	6.43	0.443	.381	0.786	2.08	1.15
46	6.43	.443	.381	.317	2.16	1.35
40	6.80	6.03	.385	3.42	2.00	1.37
38	7.06	2.52	.386	1.69	2.14	1.30
39	7.06	2.52	.386	1.43	1.69	1.21
41	6.59	10.07	.387	4.55	1.65	1.54
42	6.59	10.07	.387	4.80	2.08	1.40
43	6.85	7.82	.390	4.22	2.06	1.42
44	6.85	7.82	.390	3.91	1.68	1.46
69	7.45	5.39	.593	2.82	1.55	2.92
70	7.45	5.39	.593	2.94	1.77	2.76
27	8.87	10.75	1.13	4.36	2.27	4.69
28	8.87	10.75	1.13	4.65	2.70	4.43
25	15.66	10.36	1.51	5.23	2.28	5.44
26	15.66	10.36	1.51	5.62	2.70	5.39
S-1	1.14	1.63	1.88			6.00
81	10.54	9.33	2.08	2.87	2.65	6.59
82	10.49	9.33	2.08	3.05	2.98	6.56
S-2	1.28	1.80	3.03			2.24
S-3	1.11	2.45	3.94			0.792
S-5	7.16	7.16	5.30			.116

The original experimental numbers have been retained and they show the order in which the experiments were performed. The experiments by the sampling method (prefixed in the table by the letter "S") were carried out after those by the flow method had been completed. The preliminary experiments (1 to 24) not shown in the table were done in conjunction with H. A. Bois and experiments 25 to 37 were performed in collaboration with H. A. Young. Reasonably good agreement between the sampling and the flow methods is found by comparing experimental results of S-1 with the results of experiments 25, 26, 81 and 82. The relatively large number of experiments in the neighborhood of 0.4 *M* HCl shows the reproducibility of the flow method results and also serves to illustrate the bimolecular character of the reaction at one (HCl) when (Cl_2) and (H_2O_2) are varied. The hydrolysis of chlorine was less than one per cent. at the lowest acid concentration (0.36 *M* in Expt. 36) and was very much smaller in all other experiments.

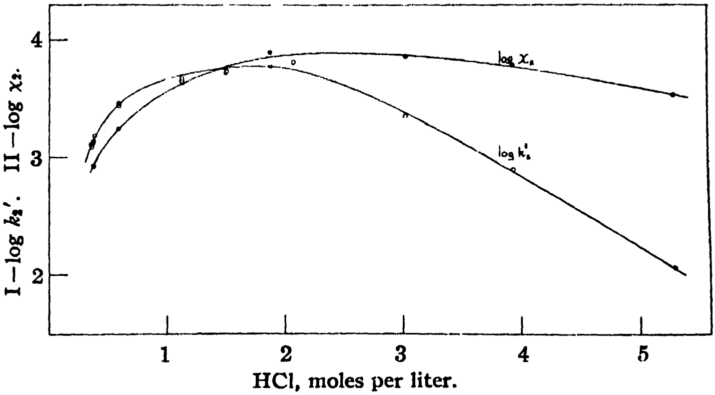

Fig. 2.

That the value of k_2' is not constant but has a maximum in the neighborhood of 2 *M* HCl is indicated by Curve I in Fig. 2, where log k_2' from Table I is plotted against (HCl). This variation, at least for (HCl) higher than 2 *M*, will be shown to be primarily a manifestation of the "secondary or equilibrium salt effect,"[11] namely, the salt effect on the chlorine hydrolysis equilibrium, Equations 3 and 5.

A relatively small part of the variation of k_2' with (HCl) is accounted for by the trichloride correction (Equation 7) expressed by means of the factor (ΣCl_2)/(Cl_2). This factor can be calculated from the relation,

$$(\Sigma Cl_2)/(Cl_2) = 1 + K_{Cl_3^-}\gamma_{Cl_2}m_{Cl^-} \qquad (8)$$

where $K_{Cl_3^-} = (Cl_3^-)/m_{Cl^-}(Cl_2)\gamma_{Cl_2}$ is an equilibrium constant specially defined[13] for the reaction, $Cl_2 + Cl^- \rightleftharpoons Cl_3^-$. m_{Cl^-} is the "molality" of chloride ion in moles per 1000 g. of water, and γ_{Cl_2} is the activity coefficient of chlorine as defined by Lewis and Randall.[12] The values of

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(11) (a) Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, 1927; (b) Livingston, "Introduction to Chemical Catalysis in Homogeneous Systems," *J. Chem. Ed.*, **7**, 2887 (1930); (c) La Mer, *Chem. Rev.*, **10**, 179 (1932); (d) Liebhafsky, This Journal, **54**, 1803 (1932), Footnote 15.

(12) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., New York, 1923.

$(\Sigma Cl_2)/(Cl_2)$ and of k_2 at various concentrations of hydrochloric acid have been calculated by means of Equations 7 and 8 and are listed in Table II. The value of $K_{Cl_3^-} = 0.17$ for hydrochloric acid solutions at 25° was obtained from the data of Sherrill and Izard[13] and the activity coefficient of chlorine, γ_{Cl_2}, was calculated by means of the Debye–McAuley law[14] for non-electrolytes, $\log \gamma = c\mu$, where μ is the ionic strength[12] expressed in terms of moles/1000 g. of water. The value of the constant $c = 0.02$ for hydrochloric acid solutions at 25° was obtained from unpublished work of M. H. Gorin of this Laboratory, and it agrees well with similar data published later by Sherrill and Izard.[13]

TABLE II

VALUES OF $[(Cl_2) + (Cl_3^-)]/(Cl_2)$ AND OF k_2 IN HYDROCHLORIC ACID SOLUTIONS AT 25°

HCl, mole/liter	0	0.5	1.0	2.0	3.0	4.0	5.0
$(\Sigma Cl_2)/(Cl_2)$	1	1.09	1.18	1.39	1.63	1.90	2.20
k_2 (10^{-3})		2.39	5.40	7.30	3.82	1.31	0.39

In order to allow for the "equilibrium salt effect," the concentration of HOCl (*cf.* Equation 4) must be calculated from the chlorine hydrolysis equilibrium expression $K = a_{HOCl}a_{H^+}a_{Cl^-}/a_{Cl_2}a_{H_2O}$, defined in terms of the "activities"[12] of the substances involved. Since the activity coefficients for HOCl are not known it will be convenient to assume that $(HOCl) = a_{HOCl}$. This assumption is not unreasonable inasmuch as concentrations do not usually differ greatly from activities in the cases of neutral substances.

The rate law for Equation 1 will now be given by the equation

$$-d(H_2O_2)dt = \kappa_2(H_2O_2)(HOCl) = \chi_2(H_2O_2)\, a_{Cl_2}a_{H_2O}/a_{H^+}a_{Cl^-}] \tag{14a}$$

where

$$\chi_2 = \kappa_2 K \tag{14b}$$

Comparison of Equation 14 with Equations 6 and 7, yields

$$\chi_2 = k_2' \frac{(Cl_2)\, a_{H^+}a_{Cl^-}}{a_{Cl_2}\,(H^+)(Cl^-)\, a_{H_2O}} \frac{(\Sigma Cl_2)}{(Cl_2)} \tag{15}$$

Since in any given reaction mixture $(Cl_2)/m_{Cl_2} = (H^+)/m_{H^+}$

$$\chi_2 = k_2' \frac{m_{Cl^-}\gamma^2_{\pm HCl}}{(Cl^-)a_{H_2O}\gamma_{Cl_2}} \frac{(\Sigma Cl_2)}{(Cl_2)} \tag{16}$$

Values of χ_2 were calculated from Equation 16 for a number of representative experiments using the results of Table II for $(\Sigma Cl_2)/(Cl_2)$ and data of Randall and Young[15] for the activities of hydrochloric acid and water. The values of χ_2 are given in Table III and are plotted in Fig. 2 (Curve II).

A comparison with Curve I indicates that while below 2 *M* hydrochloric acid there still exists a rapid decrease of χ_2 with decreasing (HCl), above

(13) Sherrill and Izard, THIS JOURNAL, **53**, 1667 (1931).

(14) Debye and McAuley, *Physik. Z.*, **26**, 22 (1922).

(15) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

TABLE III

CALCULATION OF χ_2

Run	$k_2'(10^{-3})$	(HCl)	m_{HCl}	$\gamma_{\pm HCl}$	a_{H_2O}	γ_{Cl_2}	$\chi_2(10^{-8})$
65	1.38	0.38	0.38	0.76	0.99	1.02	0.85
69	2.82	.59	.59	.76	.98	1.03	1.77
27	5.10	1.13	1.15	.84	.96	1.06	4.31
S-1	6.10	1.88	1.95	1.00	.92	1.09	7.90
S-2	2.38	3.03	3.22	1.39	.85	1.16	7.20
S-3	0.79	3.94	4.28	1.90	.79	1.22	6.20
S-5	.116	5.30	5.92	3.15	.68	1.30	3.39

that concentration of the acid the value of χ_2 remains practically constant; in other words, in this region of high (HCl) the difference between Curves I and II is satisfactorily explained by the equilibrium salt effect on Reaction 1.

This "salt effect" is further demonstrated by an additional set of experiments in which (H^+) and (Cl^-) were varied independently at a constant value of the ionic strength, approximately 5 mole/liter. Exact results can scarcely be expected since the calculations of χ_2, Table IV, involve the application of the laws listed below which are strictly valid only at low ionic strengths.

γ_{HCl} and a_{H_2O} at any ionic strength are equal, respectively, to γ and a of these substances in a solution of pure hydrochloric acid of the same ionic strength. γ_{Cl_2} was calculated from the Debye–McAuley law[14] with the aid of a further assumption that for a mixture of electrolytes, $\log \gamma_{Cl_2} = c_1\mu_1 + c_2\mu_2 + \ldots c_i\mu_i$, where μ_i is the contribution to the total ionic strength of the particular electrolyte i. The values of c_i as compiled by M. H. Gorin are: $c_{HCl} = 0.02$; $c_{HClO_4} = -0.02$; $c_{NaCl} = 0.11$; $c_{NaClO_4} = 0.06$; $c_{NaNO_3} = 0.03$.

TABLE IV

RESULTS AT CONSTANT IONIC STRENGTH AT 25°

Run	(H^+)	(Cl^-)	(H^+)(Cl^-)	μ in[c] m/liter	f[a]	$\gamma_{\pm HCl}$	$10 \times a_{H_2O}$	$10^3 \times K_{Cl_3^-}$[b]	γ_{Cl_2}	$\frac{(\Sigma Cl_2)}{(Cl_2)}$	k_2' (10^{-2})	χ_2 (10^{-2})
S-17	2.08	2.08	4.33	5.01	1.22	3.30	6.84	7.1	1.84	1.33	3.70	52.3
S-10	2.07	3.05	6.31	5.00	1.17	3.12	6.78	7.2	2.05	1.53	4.75	59.2
S-11	2.07	4.00	8.27	4.97	1.14	2.88	6.96	7.4	2.26	1.76	5.00	52.4
S-13	2.04	4.95	10.10	4.95	1.11	2.76	7.06	7.4	2.52	2.02	5.25	50.0
S-14	2.94	1.96	5.75	4.90	1.22	3.14	6.74	8.7	1.42	1.30	3.35	52.5
S-15	3.98	2.04	8.11	4.95	1.21	3.16	6.74	11.8	1.18	1.34	1.68	34.2
S-16	4.95	2.02	10.00	4.95	1.20	3.14	6.74	17.0	0.95	1.39	1.16	29.8
S-22	0.414	0.414	0.171	4.91	1.19	3.05	6.84	5.5	1.85	1.05	6.80	59.5
S-20	.210	.803	.169	4.95	1.18	3.12	6.79	5.3	2.13	1.11	6.15	54.3
S-21	.748	.198	.148	4.91	1.21	3.13	6.75	5.7	1.77	1.02	5.30	53.8

[a] The factor "f" when multiplied by concentration in moles per liter gives "molality," or moles per 1000 g. of water; it was calculated from the specific gravities of the reaction mixtures.

[b] The results of Sherrill and Izard[15] indicate great variations in the value of $K_{Cl_3^-}$ with (Na^+). For reaction mixtures containing this ion empirical values of the constant given by these authors have been used.

[c] Added electrolytes in the various experiments are as follows: in S-17 $NaClO_4$; in S-10 and S-11 $NaClO_4$ and NaCl; in S-14 and S-15 $NaClO_4$ and $HClO_4$; in S-16 $HClO_4$; in S-22 $NaNO_3$; in S-20 $NaNO_3$ and NaCl; in S-21 $NaNO_3$ and $HClO_4$.

The results of this set of experiments (Table IV) are shown to be in agreement with those of the previous set (Table III) when the values of log χ_2 taken from both tables are plotted against the square root of the activity of HCl, $\sqrt{a_{HCl}} = \sqrt{a_{H^+}a_{Cl^-}} = a_{\pm HCl}$, in Fig. 3. All the results fall on a well-defined curve with the exception of two, Runs S-15 and S-16, which are characterized by high ($HClO_4$). This deviation can, perhaps, be accounted for by the approximate nature of the assumptions (*cf.* preceding paragraph) used in calculating χ_2.

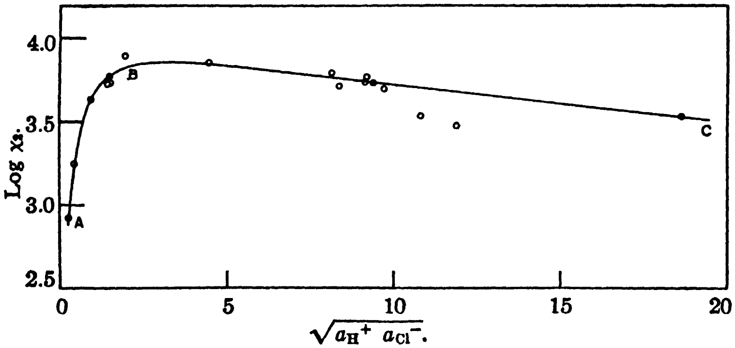


Fig. 3.

In the region BC of Fig. 3, in which the value of the product, $a_{H^+}a_{Cl^-}$, changes 90-fold (from 4 to 360), the value of k_2' changes 55-fold (from 6000 to 110) while the value of χ_2 undergoes only a two-fold variation (from 7000 to 3500). This variation can be ascribed to the assumption involved in formulating Equation 14(a). If the average value of χ_2 is taken as $5(10^3)$ and $K = 4.84(10^{-4})$ is adopted for the hydrolysis equilibrium constant at 25° (Lewis and Randall, Ref. 12, p. 508), then the specific rate, κ_2, of the bimolecular reaction, Equation 2, can be calculated by means of Equation 14(b)

$$\kappa_2 = \frac{\chi_2}{K} = \frac{5(10^3)}{4.84(10^{-4})} = 1(10)^7 \text{ at } 25° \qquad (17)$$

Discussion of Results at Low Values of the Activity of Hydrochloric Acid.—It is evident from Fig. 3 (region AB), that, when $a_{\pm HCl}$ is less than 2, the value of χ_2 suffers a rapid decrease which cannot be explained by the equilibrium salt effect. That this decrease is a function of the activity of hydrochloric acid and not of its concentration can be shown by comparing the result of experiment S-22 (Table IV), carried out at high ionic strength, with the results previously obtained under different conditions.

The possibility that either (H^+) or (Cl^-) has a specific effect on the rate is eliminated by the results of Experiments S-20, S-21 and S-22 (Table IV). Although individual concentrations of H^+ and Cl^- ions are different, the

TABLE V

RELATION OF χ_2 TO ACTIVITY OF HYDROCHLORIC ACID

	Ionic strength	$\sqrt{(H^+)(Cl^-)}$	$\sqrt{a_{H^+}a_{Cl^-}}$	$\chi_2(10^{-2})$
Run S-22	4.91	0.414	1.50	59.5
From Fig. 2	0.414	.414	0.097	9.55
From Fig. 2	1.65	1.65	1.53	64.0

activities of hydrochloric acid and therefore the values of χ_2 in the three experiments are nearly the same. Similar evidence is obtained from the results of additional experiments given in Table VI.

TABLE VI

THE EFFECT OF VARYING THE PRODUCT $(H^+)(Cl^-)$ ON THE VALUE OF k_2' AT 25°

Run	$(H_2O_2)10^3$	$(\Sigma Cl_2)10^3$	(H^+)	(Cl^-)	$(H^+)(Cl^-)$	μ in m/l.	$k_2'(10^{-3})$	Added electrolyte
71	7.78	6.42	0.256	0.607	0.155	0.607	1.36	NaCl
72	7.78	6.42	.256	.607	.155	.607	1.34	NaCl
73	8.01	6.51	.611	.257	.157	.611	1.39	$HClO_4$
74	8.01	6.51	.611	.257	.157	.611	1.39	$HClO_4$
From Fig. 2 for comparison			.396	.396	.156	.396	1.50	
			.609	.609	.370	.609	2.95	
61	6.88	6.70	.589	.198	.117	.589	1.05	$HClO_4$
62	6.88	6.70	.589	.198	.117	.589	1.08	$HClO_4$
From Fig. 2 for comparison			.342	.342	.117	.342	1.10	
			.589	.589	.347	.589	2.80	
75	7.78	6.76	.512	2.02	1.03	2.02	4.33	NaCl
76	7.78	6.76	.512	2.02	1.03	2.02	4.17	NaCl
From Fig. 2 for comparison			1.015	1.015	1.03	1.015	4.70	
			2.02	2.02	4.08	2.02	5.80	

This series of experiments consists of three groups. Since in each group the ionic strength is relatively small and nearly constant, it is possible to use the product $(H^+)(Cl^-)$ instead of $a_{H^+}a_{Cl^-}$, and k_2' instead of χ_2, for the purpose of comparison. In each group it is shown that the value of k_2' depends primarily on the value of the product $(H^+)(Cl^-)$, and that a change in ionic strength at constant value of the product has only a small effect, proving that the variation of χ_2 with the activity of hydrochloric acid is not the ordinary kinetic salt effect[11d] but has another significance. In terms of the postulated mechanism this result represents a decrease in the specific rate, κ_2, of the rate determining step, Equation 2. In the region AB, Fig. 3, the value of κ_2 (*cf.* Eq. 14b) changes from $7500/4.8(10^{-4}) = 1.5(10^7)$ to $850/4.8(10^{-4}) = 1.7(10^6)$, a nearly ten-fold decrease for a corresponding change in the value of $a_{H^+}a_{Cl^-}$ from 4.0 to 0.16. In another investigation begun in this Laboratory the above decrease was found to extend to very low activities or concentrations of hydrochloric acid, or to the coincidentally high concentrations of HOCl. A direct measurement of the rate of the reaction between HOCl and hydrogen peroxide yielded an amazingly small value for the specific rate of this bimolecular reaction, varying between 14 and 2000, depending on the (HCl) and other conditions of the experiment. No kinetic explanation of this phenomenon can as yet be offered.

Effect of Temperature.—Additional measurements of the rate of Reaction 1 were performed by means of the sampling method at 10 and 0.6°. The results, together with values at 25° taken from Fig. 2, are summarized in Table VII.

TABLE VII

THE VARIATION OF k_2' WITH THE TEMPERATURE

(HCl)	k_2'			(HCl)	k_2'		
	25°	10°	0.6°		25°	10°	0.6°
0.414	1580	530		1.99	5300	2000	
.408	1580		320	2.06	5150		900
.998	4580	1720		4.11	590	165	
.986	4500		1030	3.89	795		105

The over-all heat of activation, Q_1, of Reaction 1, in the region in which χ_2 remains nearly constant (2 M HCl and above) was calculated to have an average value of 12,000 ± 2000 calories; in the region of the rapid decrease of χ_2 it was somewhat smaller, 11,000 ± 2000 cal.

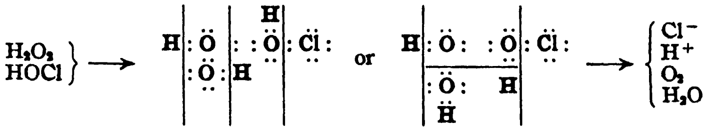
The value of Q_2, or the heat of activation of Reaction 2, is obtained by subtracting from Q_1 the value of ΔH, the heat of reaction for the hydrolysis of chlorine. The value of ΔH as given by Lewis and Randall (Ref. 12, p. 508) undergoes a considerable variation with the temperature, from 10,000 cal. at 0° to 6000 cal. at 25°, and the value of Q_1 should exhibit a corresponding decrease if the assumed mechanism is correct. However the present data at 0.6 and 10° are not accurate enough to test this prediction.

If 8000 cal. be taken as the average value of ΔH, the value of $Q_2 = 12,000 - 8000 = 4000 \pm 2000$ cal. and the change of the specific rate, κ_2, of the bimolecular reaction with the temperature (*cf.* Equation 17) can be given approximately by the expression $\kappa_2 = 10^{10}e^{-4000/RT}$ where $10^{10 \pm 1.5}$ is the order of magnitude of the Arrhenius constant.

A Possible Detailed Mechanism.—We consider the conclusion that the reaction between H_2O_2 and HOCl is bimolecular to be a definite result; and realize that an attempt to select a detailed mechanism for a reaction that takes place in the presence of water molecules must be regarded as highly speculative. Nevertheless, it is of interest to apply to this reaction the new method of attack recently proposed by Olson.[16] Each of the reacting molecules has seven pairs of valence electrons which presumably form a tetrahedron around the oxygen or chlorine kernel. The new idea is that the separation of Cl^- (with eight electrons) takes place gradually as the hydrogen peroxide molecule approaches the HOCl molecule, and supplies a pair of electrons (on one of the oxygen atoms of hydrogen peroxide) to form a new bond at the face of the tetrahedron opposite to the chlorine;

(16) Olson, *J. Chem. Phys.*, 1, 418–423 (1933).

the separation of Cl^- and the formation of the new bond are simultaneous processes. While this "inversion" is taking place the $H_3O_3^+$ is splitting into H^+, O_2 and H_2O. The whole process may be represented diagrammatically as follows



On account of the symmetry of the $H_3O_3^+$ radical, the two diagrams represent the same process. It is thus impossible to decide whether the resulting oxygen molecule consists of two atoms from one peroxide molecule or one atom from each of the reaction molecules.

The assumption that HOCl in some of its reactions dissociates into HO^+ and Cl^- has been made by W. A. Noyes[17] and has been applied by him to the reaction with hydrogen peroxide.[18] The detailed mechanism here suggested is similar in so far as the dissociation of chlorine is concerned but denies the actual existence of HO^+ at any stage of the process.

Summary

1. The rate of the rapid reaction

$$H_2O_2 + Cl_2 = O_2 + 2H^+ + 2Cl^- \tag{1}$$

has been measured over a large (0.4 to 5.2 *M*) range of hydrochloric acid concentrations. A "flow method" was used at 25° when the activity of the acid was low, because of the high speed of the reaction. A "sampling method" was used in all other experiments.

2. The rate of the reaction was found to agree in general with the rate law predicted by Livingston and Bray[1]

$$-\frac{d(H_2O_2)}{dt} = \chi_2 \frac{(H_2O_2)\, a_{Cl_2} a_{H_2O}}{a_{H^+} a_{Cl^-}} \tag{14a}$$

When the activity of hydrochloric acid is higher than 2 *M*, χ_2 is nearly constant, and has a value of $5(10^3)$ at 25°. These results furnish further evidence that the rate-determining step for Reaction 1 involves the bimolecular reaction

$$H_2O_2 + HOCl \xrightarrow{\kappa_2} O_2 + H_2O + H^+ + Cl^-, \text{ where} \tag{2}$$
$$-d(H_2O_2)/dt = \kappa_2(H_2O_2)(HOCl)$$

3. The bimolecular reaction has the maximum specific rate, $\kappa_2 = 1(10^7)$ at 25°, when (HOCl) is 10^{-7} or less. At other temperatures the rate constant is at least approximately represented by the equation, $\kappa_2 = 10^{10 \pm 1.5} e^{(-4000 \pm 2000)/RT}$. At low concentrations of hydrochloric acid and the corresponding high concentrations of HOCl this law is not obeyed and κ_2 is much smaller.

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(17) W. A. Noyes, THIS JOURNAL, 51, 2391 (1929).

(18) Letter to W. C. Bray of May 29, 1933.

4. A possible detailed mechanism for the bimolecular reaction has been discussed.

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Phase Rule Equilibria of Acid Soaps. IV. The Three-Component System Potassium Laurate–Lauric Acid–Water[1]

BY JAMES W. MCBAIN AND MALCOLM C. FIELD

In the past no attempt has been made to study the equilibria in aqueous solutions or suspensions of acid soaps by application of the phase rule. It is not surprising that this field has been neglected, because the phases which exist are in all cases very difficult to examine by the usual means. Generally, the separation even of two isotropic liquid phases is hindered by high viscosity. The authors have kept such systems for months in a thermostat at 90°, and in most cases at the end of this period very little separation had taken place.[2] We had to develop, therefore, a completely new technique.

Previous observations on the much disputed subject of acid soaps[3] mostly consist of analyses of sediments obtained from more or less dilute soap solutions. As found by Chevreul in 1823, and confirmed by Krafft and many others, these sediments exhibit a composition intermediate between that of neutral soap and fatty acid. However, in most cases this by no means indicates the composition or even establishes the existence of acid soaps because the sodium soaps and the higher potassium soaps are themselves fairly insoluble at room temperature and the sediments may consist of chance heterogeneous mixtures of variable composition usually containing both acid soap and soap itself.[4] On the other hand, the crystalline sediments from dilute solutions of a soluble soap such as potassium laurate are unquestionably acid soaps. However, in no case had sufficient care been taken to identify and characterize these different constituents.

In the corresponding anhydrous systems the acid soaps have now been definitely characterized as well-crystallized chemical substances of definite composition, not entering into isomorphous mixtures or solid solutions. Complete phase rule diagrams have been obtained for several of these anhydrous two-component systems.[1] Likewise, the other two-component system, potassium laurate–water, was mapped out in a previous study.[5]

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(1) This is the fourth of a series of studies of acid soaps carried out at Bristol University, England, in 1925–1927. For previous references see J. W. McBain and M. C. Field, *J. Phys. Chem.*, **37**, 675 (1933); J. W. McBain and M. C. Field, and J. W. McBain and A. Stewart, *J. Chem. Soc.*, 920, 924, 928 (1933); see also J. W. McBain and A. Stewart, *ibid.*, 1392 (1927).

(2) Compare R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, **24**, 1329 (1932).

(3) See references given in the first communication of this series.

(4) Examples of such experiments leading to erroneous conclusions are R. Zsigmondy and W. Bachmann, *Kolloid-Z.*, **11**, 156 (1912); W. Prosch, *Z. deut. Öl- Fett-Ind.*, **42**, 450 (1922).

(5) J. W. McBain and M. C. Field, *J. Phys. Chem.*, **30**, 1545 (1926).

The present communication comprises systematic exploration of the three-component aqueous system for all proportions, over a range of temperature of several hundred degrees. At 370° lauric acid, water and potassium laurate are almost, but not quite, miscible in all proportions, this miscibility extending over nearly all of the three-component system, but breaking down in each of the two-component systems. As the temperature falls, miscibility rapidly decreases until most of the three-component system falls into heterogeneous mixtures of phases derived from the two-component systems, potassium laurate–water and potassium laurate–lauric acid, each of which is extended slightly into the three-component system; and the only important solubilities are those of potassium laurate in water and in melted lauric acid, respectively. Several of the phases are of great interest, such as the two immiscible conic anisotropic liquid phases, neat soap and middle soap, each of which can dissolve either fatty acid or any electrolyte. Finally, the types of equilibria and the forms of the phase boundaries are in many cases quite different from those met in phase rule studies of systems not involving soap.[6]

At room temperature solid is always present, because potassium laurate, potassium hydrogen dilaurate, and lauric acid are all separate solid phases, the two latter being almost insoluble in water. When a system is cooled from higher temperatures at which it may have existed in the form of two liquid layers, the upper one always containing much more lauric acid than the lower one, crystallization takes place from each layer, more or less separately, and often lauric acid crystals separate from the upper layer and acid soap crystals KL, HL from the lower layer. The equilibria from room temperature to 90° require further study for their representation. Those at higher temperatures are much more completely known and are the subject of the present communication.

Method of Investigation

The methods employed have been for the most part described in a series of previous communications.[7] One of them depends upon the fact that supersaturation with reference to the formation of a liquid phase or of a liquid crystalline phase cannot or does not occur.[8] This is made use of to determine the position of the boundary of the isotropic liquid (sometimes of the anisotropic liquid) by noting the temperature at which the whole of a known system just becomes isotropic or, more usually, where the whole

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(6) The validity of the application of the phase rule to a colloidal system such as this is a corollary of the fact, now carefully established, that true, reversible equilibria occur in soap solutions and that these equilibria determine all the colloidal as well as the crystalloidal constituents present. Hence a soap solution from the point of view of thermodynamics and the phase rule may be regarded as a single phase when discussing its equilibria with other solutions or solids, in spite of the presence of colloidal particles, even of several different kinds.

(7) For references see J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. physik. Chem.*, **A147**, 87 (1930).

(8) See, for example, F. W. Küster and A. Thiel, "Lehrbuch der allgemeinen, physikalischen und theoretischen Chemie," 1, 327 (1913).

of the known system has been isotropic and, on cooling to a temperature T_i, just begins to separate out droplets of another phase, anisotropic liquid. This measurement may be made with the naked eye, with or without the aid of crossed nicols. Examination of a thin layer spread out under the polarizing microscope upon a heating stage with due precautions to prevent evaporation is necessary to determine when the whole of a given system of known composition just becomes or just ceases to be wholly anisotropic. Such microscopic examination is invaluable for determining whether a given system is homogeneous or heterogeneous.

Another method of determining points on the boundaries of the isotropic (or anisotropic) phase is to determine the temperature T_c at which on slow heating with good stirring the last traces of crystal dissolve completely to form one homogeneous isotropic liquid. The reverse process, cooling, is valueless on account of supersaturation.

In a few cases direct analyses of homogeneous samples of given phases were possible by decomposing with a known volume of standard aqueous sulfuric acid, and, after adding chloroform to dissolve the free fatty acid and separating the two layers, titrating the aqueous layer with sodium hydroxide, and the chloroform layer with alcoholic sodium hydroxide in the presence of excess of boiled out alcohol, using phenolphthalein as indicator.

The potassium laurate and lauric acid were those used in the study of the two-component systems.[9]

Series of systems were made up by weight in sealed glass tubes, each with the same concentration of potassium laurate (measured in weight normality, molality), and various concentrations of lauric acid. They were heated until the contents formed a homogeneous, isotropic liquid. Frequently temperatures of several hundred degrees were necessary in order to effect this. On cooling, the temperature T_i was detected by turbidity, followed in some cases at a slightly lower temperature by formation of visible globules of the second phase suspended in the first. These globules gradually separate into two or more liquid layers when the system is sufficiently fluid.

The Experimental Data

Tables I–VI contain the data obtained by the visual method. These are then plotted in the corresponding working drawings, Figs. 1–6, each of which represents a cross section through the three-dimensional phase rule model whose height represents temperature and whose triangular edges represent the three components. N_w represents weight normality, molality, the number of gram equivalents per 1000 grams of water. At 18° the systems, with the exceptions marked by footnotes, constituted a white crystalline mass, but when there were two layers the upper one solidified to a straw colored crystalline mass.

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[9] J. W. McBain and M. C. Field, *J. Phys. Chem.*, **37**, 675 (1933).

The Equilibria in Tables I–VI and Figs. 1–6.—Three distinct types of equilibria between liquid and liquid crystalline phases have been identified.

(a) Equilibria between homogeneous anisotropic middle soap and homogeneous isotropic soap solutions. These are only observed in the

TABLE I

DESCRIPTION OF THE AQUEOUS SYSTEMS 0.25 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.2564	Cloudy liquid, no separation into 2 layers	161.7
.5016	Ditto, very viscous	181.0
.7408	Ditto, very viscous	166.0
.9963	Two isotropic liquid layers	222.0
1.499		236.0

TABLE II

DESCRIPTION OF THE AQUEOUS SYSTEMS 0.50 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.3035	Cloudy, fairly mobile liquid; no layer separation	125.0
.4989	Ditto, but incomplete layer separation	156.0
1.012	Cloudy viscous liquid, droplets of one phase suspended in the other giving an appearance of anisotropic liquid crystals	183.0
1.498	Cloudy viscous liquid, incomplete layer separation	186.3
1.758		179.0
1.987	Two isotropic liquid layers	180.7
2.245		195.0
2.496	Appeared to yield three liquid layers, the upper and lower isotropic and the middle cloudy	203.0
2.746		210.5
2.986		217.0
4.995	Cloudy viscous liquid droplets of one phase suspended in the second. No separation	239.0

TABLE III

DESCRIPTION OF THE AQUEOUS SYSTEMS 1.00 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.2605	Homogeneous, isotropic liquid	None[a]
.5079	Cloudy viscous liquid, no separation of phases	121.5
.9924	Ditto, simulating anisotropic liquid crystals	162.5
2.005	Ditto, field lights up between crossed nicols[b]	182.5
2.620	Cloudy viscous liquid, no separation of the phases. Simulates anisotropic liquid crystals	172.5
3.007	Incomplete two liquid layer formation	114.0
3.510		138.5
3.990	Two isotropic liquid layers	157.0
4.971		180.0
6.977		206.8

[a] Isotropic until the crystalline phase separated.

[b] A well-known property of light reflected at interfaces in certain emulsions of two (ordinary) liquids.

TABLE IV

DESCRIPTION OF THE AQUEOUS SYSTEMS 2.00 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.4965	Homogeneous, isotropic liquid	None[a]
1.011	Cloudy viscous liquid, two-phases but no separation	148.0
2.012	Ditto, simulates anisotropic liquid	180.3
2.975	Ditto, has consistency of vaseline	182.0
4.000		164.7
4.483	Turbidity appears due to an extremely finely divided solid in isotropic liquid	92.0
5.002	Homogeneous, isotropic liquid, but on cooling below 90° like above	86.5
5.254		80.3
5.511		81.0
5.996		85.0
6.466	Cloudy, fairly mobile, two-phase system. No separation	96.5
7.001		110.0

[a] Isotropic until the crystalline phase separated.

TABLE V

DESCRIPTION OF THE AQUEOUS SYSTEMS 3.00 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.000[a]	Homogeneous, rigid, liquid crystalline middle soap	151.0
.4004[b]	Ditto, no isotropic liquid visible	146.5
.5157[b]	Ditto, no isotropic liquid visible	137.0
.5989	Ditto, no isotropic liquid visible	128.5
.7338	Cloudy, viscous two or three-phase system, no separation	115.0
1.007	Cloudy, viscous two-phase system, no separation. Looks anisotropic	154.5
1.486		179.5
2.000		185.5
2.914[c]		187.5
4.002		179.5
4.957	Ditto, but slight separation of the phases	164.0
5.431		149.0
5.973	Cloudy, almost rigid, two-phase system, no separation of the phases. Appears anisotropic	108.0
6.460		109.0[d]
7.008	Cloudy, almost rigid two-phase system. No separation	108.0
7.850		95.0
8.664	Isotropic liquid	82.0[d]
9.731	Isotropic liquid	84.0[d]

[a] At 18°, same as at 90°. [b] At 18°, fine hair-like needle crystals in bunches radiating from a central nucleus. [c] At 18°, two distinct layers of white crystals separated. Upper layer two-thirds and lower one-third by volume. [d] The turbidity temperature seems to be due in this case to an extremely finely divided solid phase of crystalline nature.

more concentrated soap systems, such as 3 and 4 N_w potassium laurate. Rigidity is characteristic of the middle soap phase; and on cooling a heterogeneous system containing middle soap and isotropic solution, the viscosity increases rapidly as the amount of isotropic solution decreases,

TABLE VI

DESCRIPTION OF THE AQUEOUS SYSTEMS 4.00 N_w WITH RESPECT TO POTASSIUM LAURATE

N_w HL	At 90°	Turbidity temp., T_i
0.000[a]	Homogeneous, rigid, anisotropic liquid crystalline middle soap	179.0
0.3307[b]	Homogeneous, rigid, anisotropic liquid crystalline middle soap	164.5
0.4949[c]		150.5
.7439	Highly viscous two or three-phase system. One phase has the appearance of anisotropic liquid crystals No separation	150.0
.9879		176.0
1.522		196.5
1.975	Highly viscous two-phase system, simulating anisotropic liquid crystals	199.7
3.472		198.7
4.987		182.0
6.445		152.0

[a] At 18°, same as at 90°. [b] At 18°, as at 90° plus traces of hair-like needle acid soap crystals. [c] At 18°, two phases, white crystals and anisotropic middle soap.

until the whole system becomes quite rigid when the homogeneous middle soap region is reached.[10]

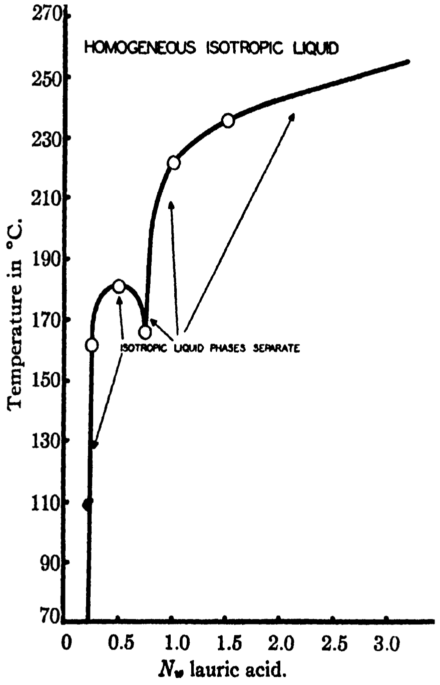

Fig. 1.—Lower boundaries of the isotropic aqueous phase containing 0.25 N_w potassium laurate.

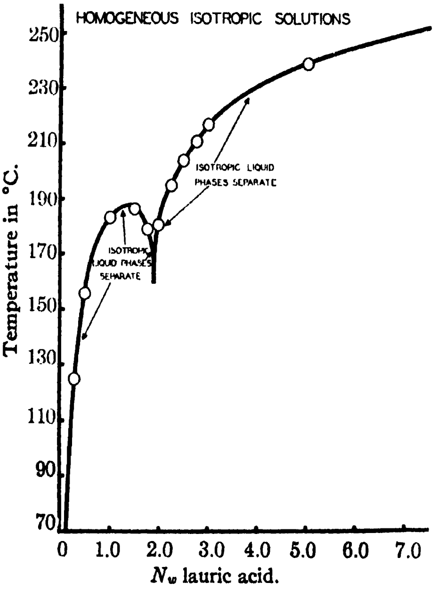

Fig. 2.—Lower boundaries of the isotropic aqueous phase containing 0.5 N_w potassium laurate.

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(10) For systematic measurements of the rigidity or structural viscosity of middle and neat soap, see J. W. McBain and O. O. Watts, *J. Rheol.*, **3**, 437 (1932).

The middle soap region is very much smaller in the system potassium laurate–lauric acid–water than in the system potassium laurate–potassium chloride–water.[5] McBain[11] gives a description of the conic anisotropic structure of middle soap for potassium laurate.

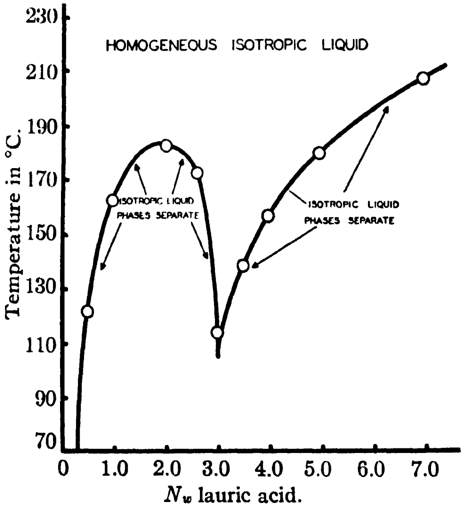

Fig. 3.—Lower boundaries of the isotropic aqueous phase containing 1.0 N_w potassium laurate.

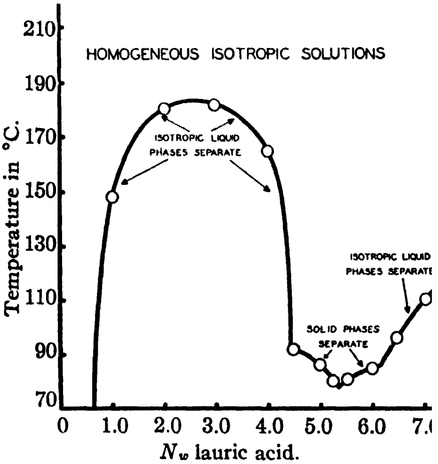

Fig. 4.—Lower boundaries of the isotropic aq ous phase containing 2.0 N_w potassium laura

(b) Equilibria between two isotropic liquid layers in which the layers separate readily. This type of equilibrium (analogous to the two layer formation, nigre–lye, met with in the salting out of soaps) occurs in the presence of excess lauric acid, which is the chief constituent of the upper layer; the lower layer is essentially a dilute aqueous solution of soap in which small quantities of fatty acid are dissolved. Certainly there is no reason to suppose that acid soaps exist in the liquid condition, especially above 91°, which is the decomposition or transition temperature of the acid soap in the solid state.

(c) Equilibria between two (apparently) isotropic liquids which scarcely ever separate owing to their being highly viscous. These are the most typical systems met with in the study of acid soaps. They are very similar to the anisotropic neat soap systems[12] in their properties although they are less rigid. A noteworthy feature is that in polarized light they exhibit double refraction, and yet, in the cases where separation of the two phases has been obtained, the two layers produced are isotropic. The anisotropic appearance is due to the polarization of light reflected at the surfaces of globules of one phase suspended in the other.

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(11) J. W. McBain, *Nature*, **114**, 49 (1924).

(12) Compare J. W. McBain and W. J. Elford, *J. Chem. Soc.*, 421 (1926).

The Triangular Diagrams.—The boundaries of the two isotropic liquid phases which can exist in the three-component system may be deduced, for representative temperatures, from the working graphs of Figs. 1–6. It is therefore possible from these numbers to draw isotropic boundaries for all temperatures up to 250° and this is done in Fig. 7.

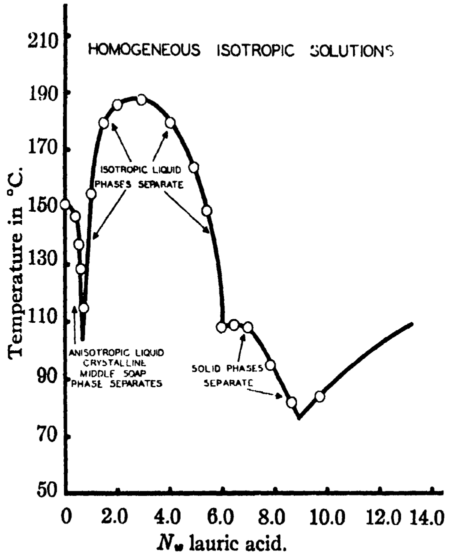

Fig. 5.—Lower boundaries of the isotropic aqueous phase containing 3.0 N_w potassium laurate.

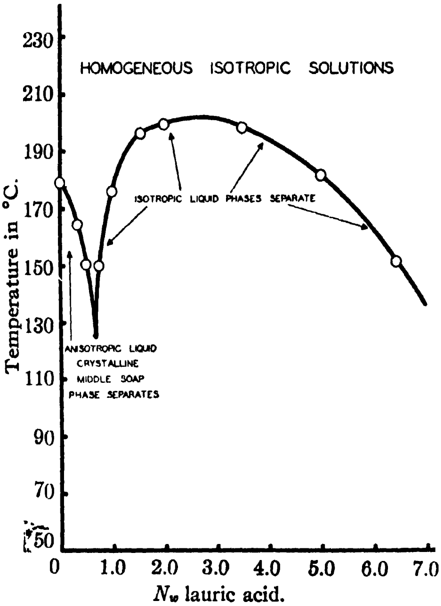

Fig. 6.—Lower boundaries of the isotropic aqueous phase containing 4.0 N_w potassium laurate.

For convenience of reference the two isotropic liquid phases are referred to as A and B, respectively. The existence of phase A is a proof that fatty acid dissolves in soap solutions,[13] although the internal constitution of these solutions has still to be accorded detailed investigation. Presumably they contain neutral colloid, ionic micelle and simple ions and molecules. The ready solubility of fatty acid in aqueous soap solutions, which at sufficiently high temperatures becomes complete miscibility, when compared with the immiscibility of fatty acid with water, can only be due to interaction between the dissolved soap and the fatty acid. This lends further support to our long maintained view that acid soap and not free fatty acid is the chief product of hydrolysis in soap solutions.

Phase B is the anhydrous solution of soap in fatty acid, which can dissolve water in curiously restricted fashion to form, at first, a narrow curved tongue whose base widens rapidly with increase of temperature and whose tip becomes remarkably elongated until just below 180° it has reached phase A. At all higher temperatures phases A and B are thus bridged, the bridge widening until at 370° it almost fills the diagram.

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[13] See also C. Bergell and N. Baskin, *Seifensieder-Ztg.*, **56**, 157 (1929)

Liquid B is generally slightly yellowish because any colored impurity goes into it rather than into the more aqueous layer A.

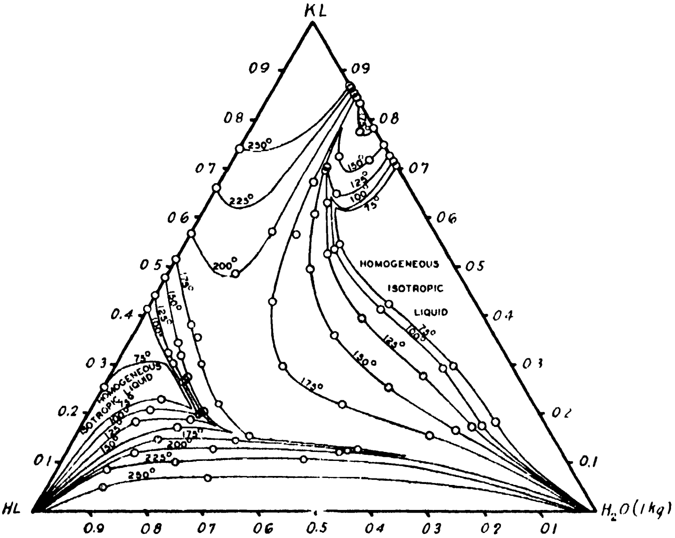

Fig. 7.—The boundaries of homogeneous isotropic liquid phases in the system potassium laurate–lauric acid–water. Isotherms for temperatures at intervals of 25°, from 75 to 250°.

Our triangular diagrams here and in previous studies of soap resemble those of Willard Gibbs with the exception that the unit of weight is not the gram but that two corners represent one gram molecular weight of lauric acid and potassium laurate, respectively, and the third corner is one kilogram of water. Intermediate points represent weights of each directly proportional to their nearness to these three corners. The total composition of the system lies upon a straight line connecting the points representing the composition at the two phases. Hence all tie lines are straight. Following previous usage, all compositions are represented in terms of "fractional proportions" of the three respective units, the whole adding up to unity for each point in the three-component system.

It will be noted that since the same units are here used as in studies of the three-component systems, soap–water–electrolyte, the triangular space model for that three-component system has one face in common with the present three-component system, namely, the two-component system soap–water. This is of very great assistance in identifying the three-component phases which extend out into the respective triangular prism models or, for a given temperature, triangular isotherms. We have found it useful to construct tetrahedral models (one tetrahedron for each temperature) in deducing the four-component systems potassium laurate–lauric acid–potassium chloride–water of which the four three-component systems are restricted cases and form the faces of the tetrahedra.

For lack of more precise knowledge the neat soap and the hydrated soap crystal boundaries are assumed to extend into the acid soap system in a manner similar to that in the aqueous electrolyte system.

Separation at 90°.—Thirty-three sealed up systems were placed in a thermostat at 90° for three or four months, at which time they were examined visually and carefully described with a view to identifying the nature of the phases present. In twenty-one cases there was either no separation in bulk, although the presence or absence of anisotropic liquid in the heterogeneous mixture was detectable, or in two cases the whole system formed one mobile isotropic liquid (Phase B). In the other cases there was more or less separation, sometimes into two isotropic liquids but sometimes one of the layers being definitely anisotropic. Always in the latter case, and frequently in the former, one or both of the layers was contaminated by droplets of the other. Five of these systems were analyzed in order to determine the gross composition of each layer.

TABLE VII

ANALYSES OF MORE OR LESS COMPLETELY SEPARATED TWO LAYER SYSTEMS

		A	B	C	D	E
Total composition	N_w KL	0.2525	0.04940	0.5046	0.5037	2.997
	N_w HL	1.499	1.498	1.758	2.496	1.486
Upper layer	N_w KL	4.093	11.60	1.574	3.265	3.181
	N_w HL	26.46	59.17	6.759	17.04	1.534
Lower layer	N_w KL	0.0222	0.3867	0 3242	0.1496	2.204
	N_w HL	.0410	.9738	.8800	.5715	0.7158

In systems A, B, C and D the upper layer was moderately mobile, fairly clear and straw colored, the lower layer being much more viscous, being cloudy in A but exhibiting visibly suspended droplets in the other cases. In system E the lower layer was a clear isotropic liquid, the upper four-fifths of the system being a cloudy, highly viscous, anisotropic mixture.

Separation in system A is almost perfect, exactly placing the tie line, each end of which falls on the boundary of homogeneous, isotropic liquid phase as already determined.

Separation in B and D is good as regards the upper layer, whose composition lies on the liquid boundary previously determined. The lower layer, however, is sufficiently viscous to have retained droplets of the upper layer. The analysis, therefore, gives the direction of the tie line but does not reach its extremity.

Separation in C is imperfect as regards both layers, therefore merely giving the direction of the tie line.

Separation in E has yielded only the lower phase pure, for this is a three-phase system of which the third phase is presumably neat soap.

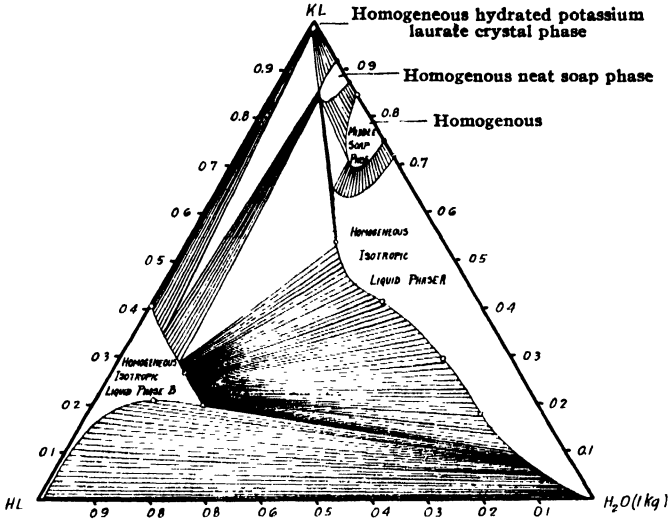
KL
Homogeneous hydrated potassium laurate crystal phase
Homogenous neat soap phase
Homogenous
Middle Soap Phase
Homogeneous Isotropic Liquid Phase A
Homogeneous Isotropic Liquid Phase B
HL
H_2O(1 kg)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 8.—Equilibria at 100°.

Discussion

Before presenting the phase rule diagrams for representative temperatures from 100 to 370°, it may be recalled that middle soap is a plastic, conic anisotropic liquid, turbid if stirred but often quite transparent. Its apparent or structural viscosity is of the order of a hundred million times that of water and greater than that of vaseline.

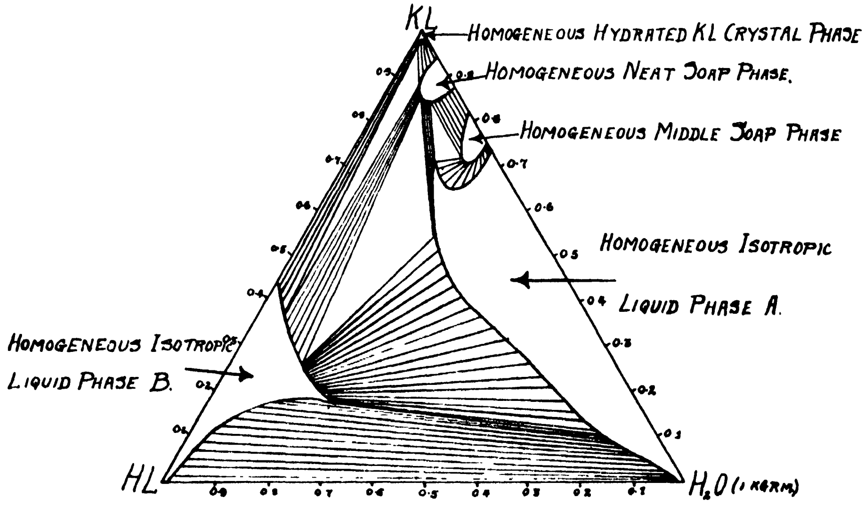
KL
Homogeneous Hydrated KL Crystal Phase
Homogeneous Neat Soap Phase.
Homogeneous Middle Soap Phase
Homogeneous Isotropic Liquid Phase A.
Homogeneous Isotropic Liquid Phase B.
HL
H_2O (1 kgm)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 9.—Equilibria at 125°.

Neat soap is also a conic anisotropic liquid, more turbid than middle soap with which it is immiscible. We (like Ferguson and Richardson[2]) were under the impression that it was less rigid than middle soap, but the quantitative examination of McBain and Watts demonstrated that it was even more rigid.

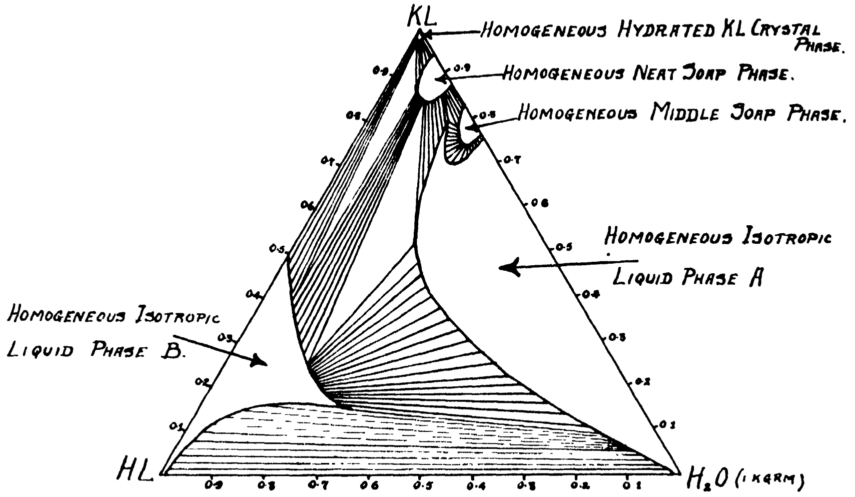
KL
Homogeneous Hydrated KL Crystal Phase.
Homogeneous Neat Soap Phase.
Homogeneous Middle Soap Phase.
Homogeneous Isotropic Liquid Phase A
Homogeneous Isotropic Liquid Phase B.
HL
H_2O (1 kgrm)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig 10.—Equilibria at 150°.

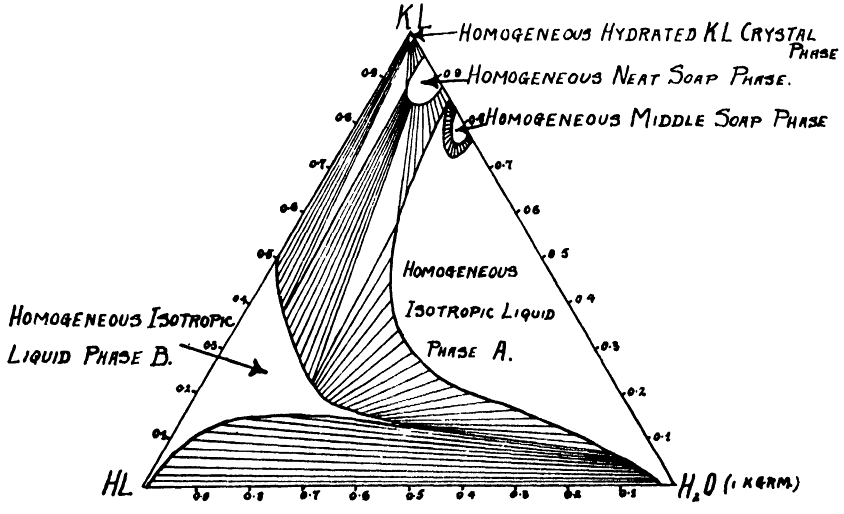
KL
Homogeneous Hydrated KL Crystal Phase
Homogeneous Neat Soap Phase.
Homogeneous Middle Soap Phase
Homogeneous Isotropic Liquid Phase A.
Homogeneous Isotropic Liquid Phase B.
HL
H_2O (1 kgrm)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 11.—Equilibria at 164°.

Crystals of potassium laurate are transparent, hexagonal lamelae, giving a silvery white paste. They are only slightly hydrated.

Figures 8–21 present the results of this investigation, outlining the equilibria met with at 100, 125, 150, 164, 175, 178, 180, 183, 200, 225, 239, 250, 275 and 370°. Of these the diagrams at 100, 175 and 250° are worked out with the most care. The notes and comments already made in this paper, together with the annotations upon the diagrams, will enable those conversant with the phase rule to read the qualitative and quantitative significance of the various equilibria, in spite of the unique and highly interesting phenomena presented.

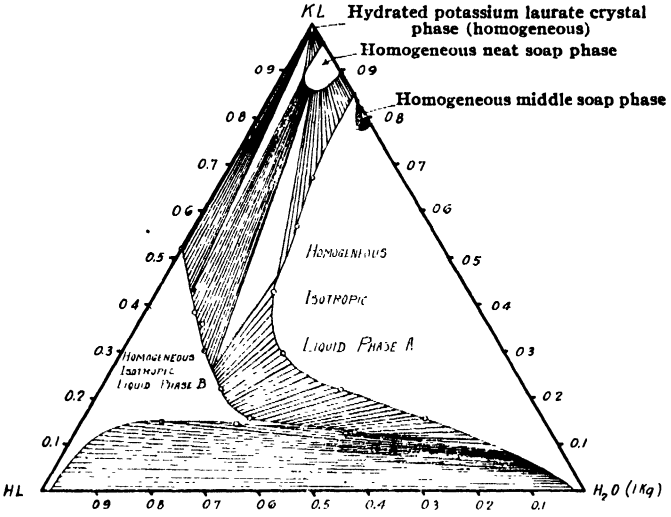
KL
Hydrated potassium laurate crystal phase (homogeneous)
Homogeneous neat soap phase
Homogeneous middle soap phase
Homogeneous Isotropic Liquid Phase A
Homogeneous Isotropic Liquid Phase B
HL
H_2O (1 Kg)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 12.—Equilibria at 175°.

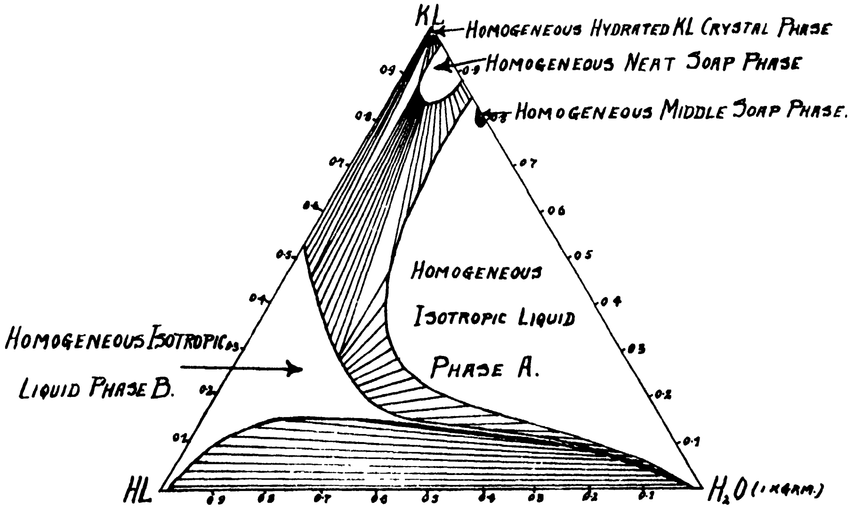
KL
Homogeneous Hydrated KL Crystal Phase
Homogeneous Neat Soap Phase
Homogeneous Middle Soap Phase.
Homogeneous Isotropic Liquid Phase A.
Homogeneous Isotropic Liquid Phase B.
HL
H_2O (1 Kgm.)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 13.—Equilibria at 178°.

At 164° the middle soap phase becomes completely surrounded by isotropic liquid phase A. At 178° the isotropic liquid phase A unites with (reaches) the liquid phase B. At 180° the middle soap phase vanishes. At 376° neat soap vanishes and only isotropic liquids survive.

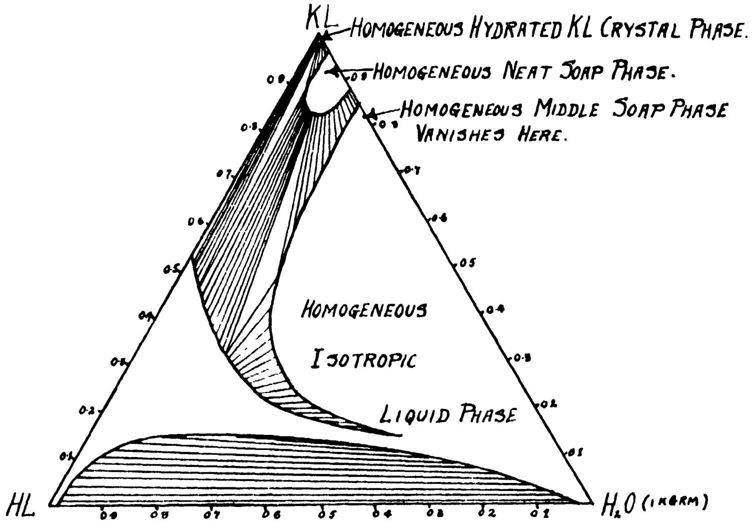
KL
HOMOGENEOUS HYDRATED KL CRYSTAL PHASE.
HOMOGENEOUS NEAT SOAP PHASE.
HOMOGENEOUS MIDDLE SOAP PHASE VANISHES HERE.
HOMOGENEOUS
ISOTROPIC
LIQUID PHASE
HL
H_2O (1 KGRM)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 14.—Equilibria at 180°.

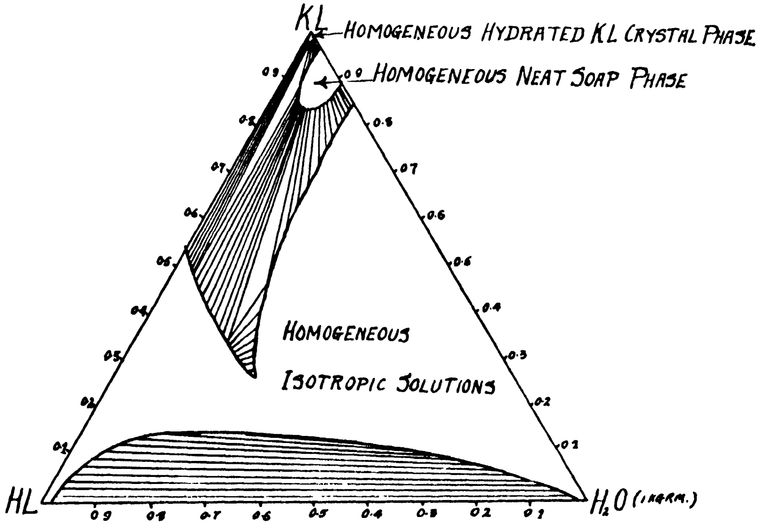

Fig. 15.—Equilibria at 183°.

It may be helpful to point out that eleven types of two- or three-phase equilibria occur at 100°, types 5 and 6 having disappeared by 175° and only types 1, 3 and 9 remaining at 250°. The types are listed as follows:

1. Two-phase equilibria between homogeneous, isotropic liquid phase A and the lower boundary of homogeneous, isotropic liquid phase B. The limiting case of these heterogeneous equilibria is between liquid lauric acid and water.

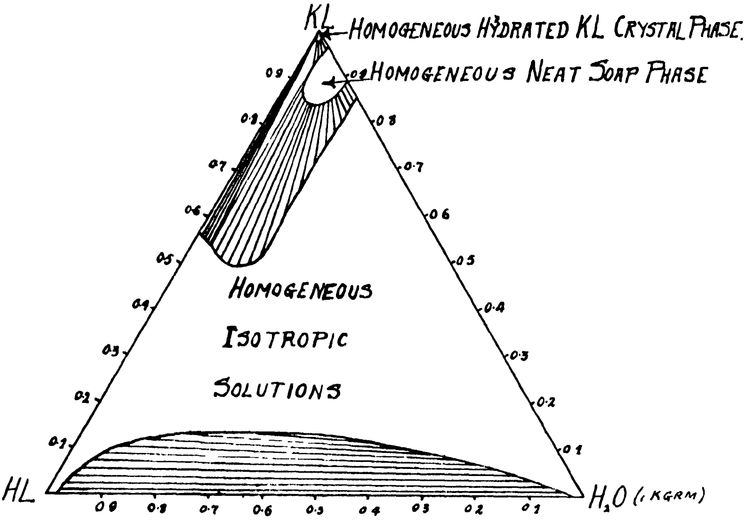
KL
Homogeneous Hydrated KL Crystal Phase.
Homogeneous Neat Soap Phase
Homogeneous Isotropic Solutions
HL
H_2O (1 kgrm)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 16.—Equilibria at 200°.

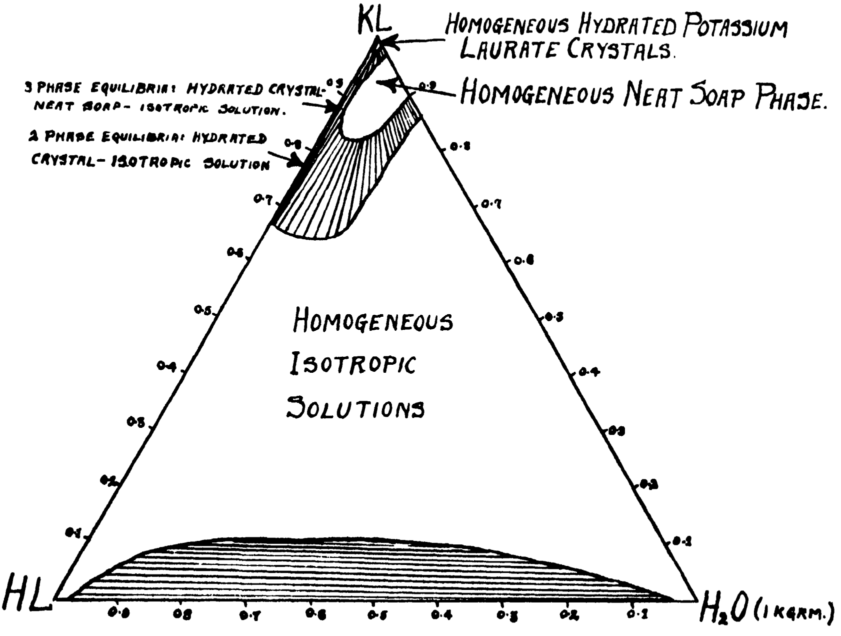
KL
Homogeneous Hydrated Potassium Laurate Crystals.
Homogeneous Neat Soap Phase.
3 Phase Equilibria: Hydrated Crystal-Neat Soap-Isotropic Solution.
2 Phase Equilibria: Hydrated Crystal-Isotropic Solution
Homogeneous Isotropic Solutions
HL
H_2O (1 kgrm.)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 17.—Equilibria at 225°.

2. Two-phase equilibria between homogeneous, isotropic liquid A and the upper boundary of homogeneous isotropic liquid B.

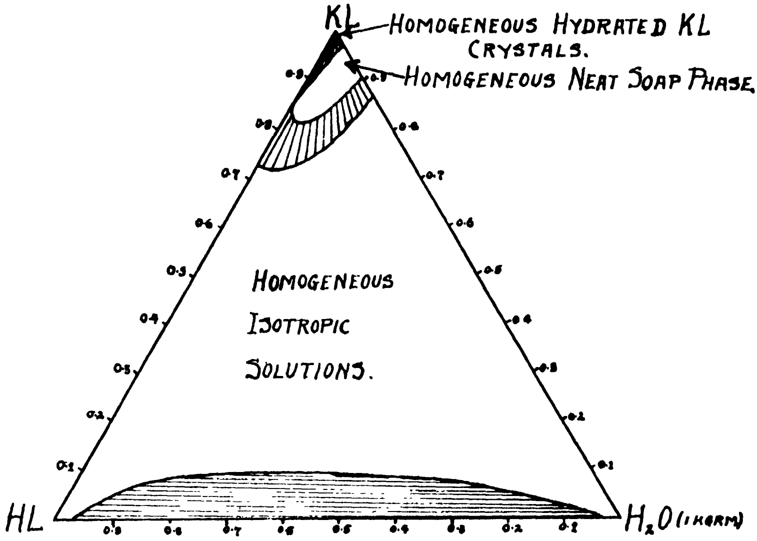
KL
Homogeneous Hydrated KL Crystals.
Homogeneous Neat Soap Phase
Homogeneous Isotropic Solutions.
HL
H₂O (1 kgm)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 18.—Equilibria at 239° at which neat soap just appears in the two-component system KL, HL.

3. Three-phase equilibria between homogeneous, anisotropic neat soap, and homogeneous, isotropic liquid phases A and B.

4. Two-phase equilibria between homogeneous, anisotropic rigid middle

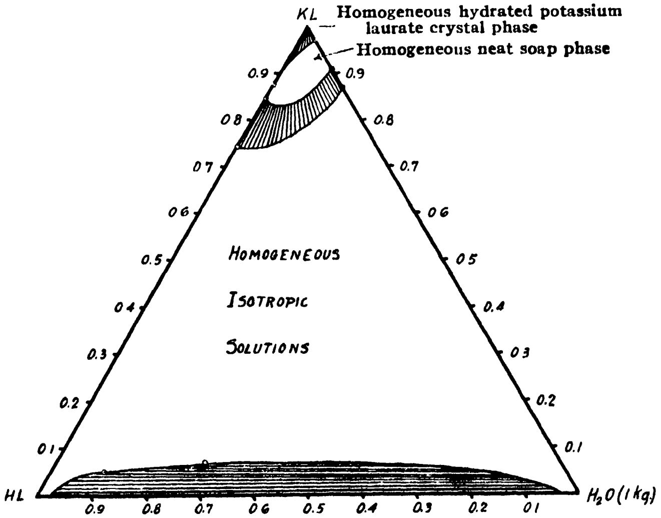
KL
Homogeneous hydrated potassium laurate crystal phase
Homogeneous neat soap phase
Homogeneous Isotropic Solutions
HL
H₂O (1 kg.)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Fig. 19.—Equilibria at 250°.

soap, and homogeneous, isotropic liquid A, the limiting case of which occurs in the absence of lauric acid.

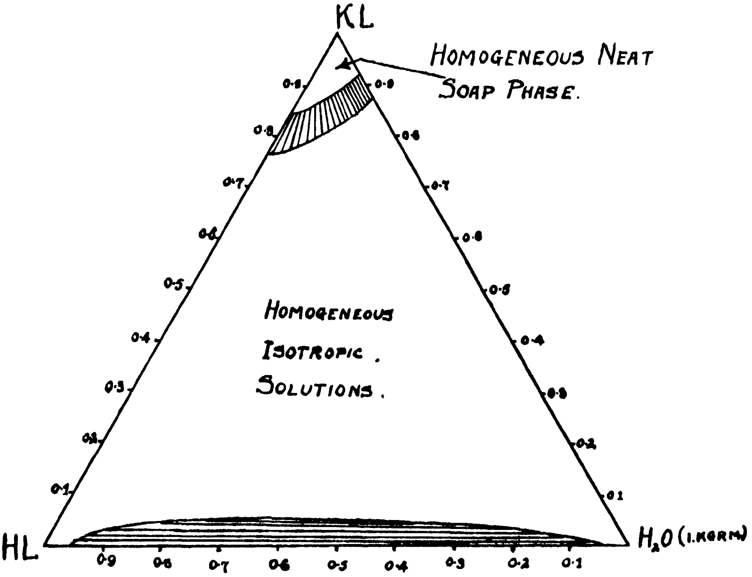
KL
Homogeneous Neat Soap Phase.
Homogeneous Isotropic . Solutions .
HL
H_2O (1 kgrm)
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1

Fig. 20.—Equilibria at 275°.

5. Two-phase equilibria between homogeneous, anisotropic neat soap, and homogeneous, anisotropic rigid middle soap, the limiting case of which occurs in the absence of fatty acid.

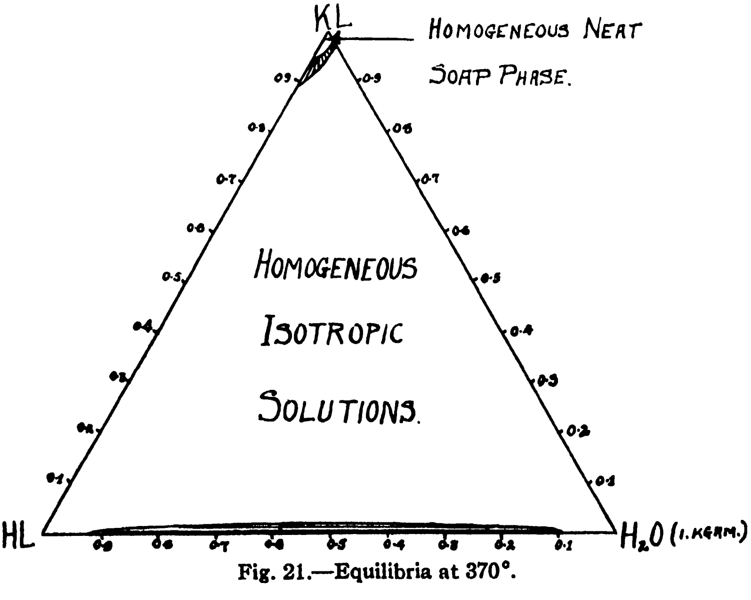
KL
Homogeneous Neat Soap Phase.
Homogeneous Isotropic Solutions.
HL
H_2O (1 kgrm.)
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1

Fig. 21.—Equilibria at 370°.

6. Three-phase equilibria between homogeneous, anisotropic plastic neat soap, homogeneous, anisotropic middle soap, and homogeneous, isotropic liquid phase A.

7. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and isotropic liquid phase A.

8. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and isotropic liquid phase B.

9. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and homogeneous, hydrated potassium laurate crystals, the limiting case of which occurs in the absence of lauric acid.

10. Three-phase equilibria between homogeneous, anisotropic, plastic neat soap, homogeneous, hydrated potassium laurate crystals, and homogeneous isotropic liquid phase B.

11. Two-phase equilibria between homogeneous, hydrated potassium laurate crystals, and homogeneous, isotropic liquid phase B, the limiting case of which occurs in the absence of water when the isotropic liquid phase B is in equilibrium with anhydrous potassium laurate.

Summary

It is attempted for the first time to map out with phase rule diagrams the equilibria existing in an aqueous three-component system of acid soaps. This is done from 100 to 370°, some remarkable and unique equilibria being exhibited.

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Solubility. XIII. The Solubility of Iodine in Certain Solvents

BY G. R. NEGISHI, L. H. DONNALLY AND J. H. HILDEBRAND

The solubility of iodine in a variety of solvents is unusually interesting because of the large number of "regular solutions"[1] it forms showing large deviations from Raoult's law. These solutions are particularly striking in the relationship they show between "regularity" and color. The investigations here described were undertaken for the purpose of including certain additional solvents: ethylene bromide, because of its high solvent power, isooctane, to compare with a normal paraffin, and two of the tetrahalides included under a comprehensive investigation now going on under the direction of the senior author,[2] *viz.*, the tetrachlorides of silicon and titanium.

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(1) J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

(2) J. H. Hildebrand and J. M. Carter, *ibid.*, **54**, 3592 (1932).

Materials and Purification

The "Reagent Iodine Merck" was dried over phosphorus pentoxide and was used without further treatment.

Eastman ethylene dibromide was washed, several times, with dilute sodium hydroxide and distilled water, shaken with calcium chloride in a sealed flask for two days and fractionally distilled three times. The first and last portions were discarded and the middle portion, boiling at 130.9–131.0° at 755 mm., was collected in a Pyrex flask, which was stoppered with a cork covered with tinfoil. It was kept in the dark.

For the purification of technical titanium tetrachloride, an all-Pyrex apparatus was employed similar to that used by Baxter and Fertig.[3] The apparatus consisted of seven 1500-cc. distilling flasks, each equipped with a fractionating column, an outlet to a vacuum line or to the atmosphere, a water condenser, and a magnetically breakable inner seal. In the fourth flask, a thermometer was hung from a platinum hook inside the projecting fractionating column so as not to touch the wall. The receiving flask was equipped with a number of inner seals and a phosphorus pentoxide tube which could be connected to a vacuum line or to the atmosphere.

The starting material was distinctly reddish-yellow, due to ferric chloride and vanadium chloride. The former is easily removed by distillation, but the latter, imparting a lemon-yellow color,[4a] necessitated refluxing for from four to six hours over dilute sodium amalgam (less than 1%) in the first two flasks. The next flask was dried by evacuating and heating several times. The seal was broken and the material was distilled over at a reduced pressure. The distillate was colorless and clear. The same procedure was followed in the successive operations, except that the boiling point of the material was determined at ordinary pressure. The first and the last portions were discarded and the middle portion obtained was colorless and clear, boiling at 135.7–135.9° at 756 mm. Particular care was taken to prevent the liquid and its vapor from coming in contact with moisture. When the liquid was distilled into the receiving flask, the phosphorus pentoxide tube was sealed off and the liquid was kept in the flask under a reduced pressure.

Technical silicon tetrachloride, which was yellow and slightly turbid, was purified in a similar apparatus. The yellow liquid, which was presumably due to iron and chlorine[4b] was refluxed twice over mercury, and then distilled in an atmosphere of dry nitrogen. The nitrogen from a commercial tank was forced successively through pyrogallol in 12 *N* technical sodium hydroxide, C. P. concentrated sulfuric acid, phosphorus pentoxide tube and a tube of glass wool, into the distilling apparatus. The first and the last portions of each distillation were discarded and the middle portion, boiling sharply at 56.9 at 750 mm., was collected. All precautions were taken to keep out the moisture during the purification.

The isooctane was 2,2,4-trimethylpentane obtained from the Ethyl Gasoline Corporation.

Apparatus and Procedure

For the solubility of iodine in ethylene bromide we used, with but slight modification, the apparatus of Hildebrand and Jenks.[5] After the chamber was dried, iodine was introduced and dibromoethane distilled into it. It was then stoppered with a ground-glass stopper and the bulb was placed in the thermostat in the rocking device. After the equilibrium was reached, the bulb was tilted so that the outlet was almost perpendicular. The stopper was replaced by the pipet and a portion of the solution was

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(3) G. P. Baxter and G. J. Fertig, THIS JOURNAL, 45, 1229 (1923).

(4a) Gmelin-Kraut's "Handbuch der anorg. Chemie," 1912, Vol. III, 1, p. 61.

(4b) Gmelin-Kraut's "Handbuch der anorg. Chemie," 1912, Vol. III, 1, 1268.

(5) J. H. Hildebrand and C. A. Jenks, THIS JOURNAL, 42, 2184 (1920).

transferred into the pipet by forcing dry air at the temperature of the bath, saturated with dibromoethane through the side tube provided with a stopcock. The construction of the bulb was such that the solid was kept away from the tip of the pipet. The bulb was kept under the surface of water in the thermostat during the filling of the pipet. When approximately 10 cc. of liquid was forced into the bulb of the pipet, it was removed, the liquid adhering to the stem was wiped off with filter paper and, after slipping on a glass tube closely fitting the stem at each end of the pipet, it was weighed, the contents washed into a flask, and titrated with sodium thiosulfate. The weights and the buret used were standardized.

For the determination of the solubility of iodine in titanium chloride an apparatus of Pyrex, as shown in Fig. 1, was used. Four of these were fused onto a Pyrex tube with a water condenser, which in turn was fused onto an inner seal connected to the receiving flask. The system was dried by repeatedly evacuating, heating and introducing dry, pure nitrogen. A steady stream of nitrogen prevented other gases from entering into the system. When the system was filled with nitrogen, each of the large bulbs was cooled with ice and salt, the projecting tube was broken off at C, and iodine was introduced into the bulb. While the stream of nitrogen was passing through, the tube was sealed off by heating about 5 cm. below C. The same procedure was followed until iodine was introduced into each of the large bulbs. The nitrogen was then shut off, the system evacuated, the seal broken and titanium chloride was distilled into each bulb. As each one was filled, it was sealed off at B.

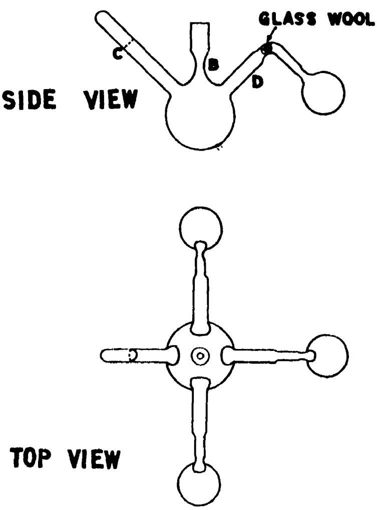

Fig. 1.

The bulb was shaken in the bath in such a way as to rock the contents back and forth along the projecting tube. The length of the tube D was sufficient to eliminate any danger of liquid in the bulb reaching a wad of glass wool in the tube. The equilibrium was approached from above in every case. When equilibrium was reached, portions of the solution were drained into the smaller bulbs by tilting. During the transferring of the solution, the whole apparatus was kept under the surface of the water. When the transfer was complete, the apparatus was taken out of the bath, immersed in ice and salt mixture and each bulb was sealed off. The neck of the smaller bulb was drawn and constricted so that very little heating was required in sealing it off. A very small amount of white substance was formed in the neck where it was heated, but any error due to this was considered negligible.

The method of analysis was similar in manipulation to that of Baxter and Fertig.[3] The small bulb was washed successively in cleaning solution and distilled water. After drying and weighing carefully, it was put in a flask with a ground glass stopper containing 500 to 750 cc. of potassium iodide solution saturated with carbon dioxide gas. After carbon dioxide was bubbled through the solution in the flask for about forty minutes to displace the air, the stopper was replaced, and the bulb was broken by shaking it violently against the thick walls of the flask. After the white cloud had disappeared, the contents was titrated with sodium thiosulfate. A steady stream of carbon dioxide was passed into the flask during the titration. It was essential to prevent all access of oxygen, since, in such a strongly acid solution, it would oxidize iodide ion. The end-point of the titration was quite sharp in spite of the presence of the white titanic acid. The broken glass pieces were collected, boiled in nitric acid to dissolve any precipitate adhering to them, transferred to a weighed Gooch crucible, dried carefully and weighed.

The apparatus and the method of analysis employed for silicon chloride were the same as above except that silicon tetrachloride was distilled in an atmosphere of nitrogen. When the small bulbs were sealed off, no white deposit was formed. When the bulb was broken in potassium iodide solution in the flask, there was only slight or no cloud formation, and the solution was practically clear.

Since blank tests made for iodine–titanium chloride checked with the theoretical results, it was thought unnecessary to make the blank test runs for the iodine–silicon tetrachloride system.

The temperature of the thermostat at 25° was kept within ±0.01° and that at 40° and above maintained within ±0.03°.

The results of the measurements are summarized in Table I, and represented graphically in Fig. 2 in comparison with published measurements in

TABLE I

SOLUBILITY OF IODINE

Temp., °C.	Wt. per cent.			Average	Mole per cent.
		Solvent, titanium tetrachloride			
0.10	1.152	1.153		1.153	0.8633
25.00	2.856	2.853	2.856	2.855	2.150
40.00	4.626	4.640	4.626	4.631	3.499
49.90	6.499	6.504	6.496	6.500	4.939
		Solvent, silicon tetrachloride			
0.10	0.2569	0.2544	0.2551	0.2555	0.1713
25.00	.7462	.7431	.7417	.7433	.4987
40.00	1.310	1.308	1.311	1.309	.8801
		Solvent, ethylene bromide			
8.00	6.707	6.496	6.467	6.557	4.925
10.00	6.792	6.851	6.886	6.850	5.161
15.00	7.875	7.843		7.859	5.937
20.00	9.139	9.086	9.058	9.091	6.895
24.80	10.38	10.38		10.38	7.895[a]
25.00	10.32	10.30	10.33	10.32	7.815
30.02	11.88			11.88	9.073[a]
34.20	13.10	13.17		13.14	10.07[a]
35.00	13.40	13.42	13.43	13.42	10.28
35.07	13.73	13.59		13.66	10.49[a]
45.00	17.45	17.42	17.43	17.43	13.51
49.60	19.18	19.05		19.12	14.89[a]
60.00	25.55	25.50	25.57	25.54	20.24
70.00	33.33	33.26		33.30	26.97
75.00	37.61	37.56		37.61	30.85
76.50	39.85			39.85	32.90[a]
78.40	42.41	42.38		42.40	35.26[a]
		Solvent, isooctane (2,2,4-trimethylpentane)			
24.92	1.302	1.303		1.303	0.5900[a]
35.00	1.922	1.915	1.917	1.918	.8711[a]

[a] Measurements by L. H. Donnally.

other solvents. Several points may be mentioned in connection with the plot. First, the solutions in titanium and silicon tetrachlorides and in isooctane fit into the family of "regular" curves previously found for all violet colored solutions and obeying rather closely the equation

$$\log N_2^i/N_2 = kN_1^2/4.575\,T \qquad (1)$$

The value of N_2^i for iodine can be calculated from the equation

$$\log N_2^i = \frac{-\Delta H}{4.575}\left(\frac{1}{T} - \frac{1}{T_m}\right) \qquad (2)$$

where ΔH, the heat of fusion per mole, is 4010 cal., and T_m, the melting point, is 387.2°. Substituting Equation 2 with these values in Equation 1 gives

$$-\log N_2 = (kN_1^2 + 876)/T - 2.262 \qquad (3)$$

TABLE II

t, °C.	Molal vol. I_2, cc.	V_1	100 N_2	k	A	V_1	100 N_2	k	A
			Solvent $TiCl_4$				Solvent $SiCl_4$		
0.1	57.6	107.8	0.863	308	24.3	111.5	0.171	501	39.7
25.0	59.0	110.5	2.150	309	23.5	115.3	.499	490	37.8
40.0	59.8	112.5	3.499	310	23.0	117.8	.880	485	36.7
49.9	60.4	113.5	4.939	308	22.3	...	...	...	...
			Mean	309	23.8			492	37.1
			Calcd.	Eq. 7	26.7				39.2
			Solvent $C_2H_4Br_2$				Solvent CS_2		
0.0	57.6	...	....	...	...	58.9	2.50	188	14.9
10.0	58.2	85.3	5.161	144	10.9	59.6	3.41	180	14.4
25.0	59.0	86.6	7.815	151	11.0	60.7	5.76	190	14.7
42.0	59.9	...	....	...	...	61.8	9.86	190	14.2
45.0	60.1	88.3	13.51	161	11.2	...	...	...	...
60.0	60.9	89.6	20.24	173	11.3	...	...	...	...
75.0	61.7	91.0	30.85	188	11.3	...	...	...	...
			Mean	163	11.1			187	14.6
			Calcd.	Eq. 7	16.0				15.1

For CCl_4, from 0 to 50°, k varies from 395 to 384; A from solubility 31.2 to 28.5; A from Eq. 7, 28.5. For C_7H_{16}, A from solubility, 40.7; from Eq. 7, 29.6.

Table II gives empirical values of k calculated from the equation which show how well the new systems fit this relation. The good agreement for the other violet solutions has been previously pointed out.

The only considerable deviation in the case of a violet solution is for ethylene bromide, shown by the smaller slope in Fig. 2, and by the increase in k from 144 at 10° to 188 at 75°. It is not possible, from the data at hand, to determine whether this is due to failure of the solution to behave "regularly," in the sense of possessing ideal entropy of mixing, or to failure to obey the simple relation of Equation 1. In other words, the change of solubility with temperature is a total differential, since both composition and temperature are changing, and a complete understanding of the system requires a knowledge of the partial differentials of the activity with respect to both variables. This may be formally expressed by writing the mathematical identity

$$\mathrm{d} \ln a_2 = \left(\frac{\partial \ln a_2}{\partial \ln \mathrm{N}_2}\right)_T \mathrm{d} \ln \mathrm{N}_2 + \left(\frac{\partial \ln a_2}{\partial T}\right)_\mathrm{N} \mathrm{d}T$$

we can set a_2 in the left-hand member equal to N_2^i and rearrange, giving

$$\frac{\mathrm{d} \ln \mathrm{N}_2^i}{\mathrm{d}T} = \left(\frac{\partial \ln a_2}{\partial \ln \mathrm{N}_2}\right)_T \frac{\mathrm{d} \ln \mathrm{N}_2}{\mathrm{d}T} + \left(\frac{\partial \ln a_2}{\partial T}\right)_\mathrm{N} \qquad (4)$$

We can measure the total differential by the solubility, but cannot evaluate either partial differential from the same data. We must measure one of them independently.

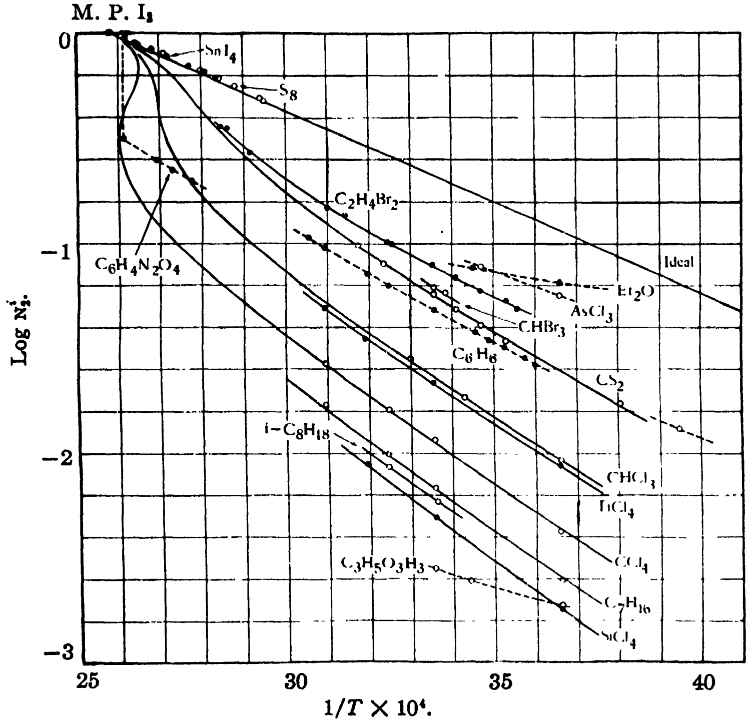

Fig. 2.—Solubilities of iodine.

It is worth noting that a regular solution may depart from Equation 1, requiring some more complex relation, such as

$$\log \frac{\mathrm{N}_2^i}{\mathrm{N}_2} = \frac{1}{4.575\,T}\left(k\mathrm{N}_1^2 + l\mathrm{N}_1^3 + \ldots\right) \qquad (5)$$

and still not diverge from the family of regular curves, provided N_2 is so small that N_1 is practically unity. Divergence in this range must be regarded as evidence of irregular entropy, and hence oriented molecules. However, when N_2 is large, as in the region between 0 and 0.1, different regular (violet?) solutions might fail to show parallel curves because of the higher coefficients of Equation 5, such as might arise from inequality in molecular volumes. It is doubtless significant that whereas carbon disulfide, which obeys the simple Equation 1 with iodine, has almost the same volume; ethylene bromide, whose solutions with iodine deviate from Equation 1, has a much larger molal volume. The tetrachlorides here used and heptane have still larger molal volumes, but the smaller concentration of iodine in their solutions in the range herein studied prevents any difference between Equations 1 and 5 coming to light.

It is possible that, in spite of the violet color, there is some approach to solvation in ethylene bromide which would be revealed by a study of the absorption spectrum over a range of temperature, as in the case of carbon disulfide.[6] Or it may be that the discrepancy is due to the polarity of the ethylene bromide. Its dipole moment is 1.4×10^{-18} e. s. u.

The relative positions of the curves for violet solutions in Fig. 2 correspond well, on the whole, with the relative values of the intermolecular forces indicated by the values[7] of $\Delta E/V$ and of $(\partial E/\partial V)_T$ shown in Table III. E denotes energy, ΔE the energy of vaporization and V the molal volume. The position of the solubility curve for a new "violet" solvent could therefore be predicted with reasonable accuracy. The minor discrepancy in the position of the curve for silicon tetrachloride with respect to the two paraffins may be connected with the differences in molal volumes. The significance of the reversed S-shape of the upper portion of the curve for carbon tetrachloride has been discussed in an earlier paper.[1]

TABLE III

RELATION OF INTERNAL PRESSURE TO NON-IDEALITY OF IODINE SOLUTIONS

Solvent	k	$(\partial E/\partial V)_T$, atm.	$\frac{\Delta E}{V}$, atm.	Solvent	k	$(\partial E/\partial V)_T$, atm.	$\frac{\Delta E}{V}$, atm.
$SiCl_4$	492	2554	2390	CS_2	190	3670	4120
i-C_8H_{18}	466	...	2040	$CHBr_2$	168	4450	...
C_7H_{16}	450	2510	2310	$C_2H_4Br_2$	151	4420	4040
CCl_4	389	3310	3015	S_8	0	...	...
$TiCl_4$	309	3430	3140	SnI_4	0	...	4220
$CHCl_3$	300	...	3520	I_2	0	...	...

An interesting quantitative treatment of this problem has been given by Scatchard,[8] who has derived the equation

$$RT \log \frac{N_2^i}{N_2} = A V_2 \left(\frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \right)^2 \tag{6}$$

This reduces to Equation 1 when $V_1 = V_2$, giving $AV = 4.575\ k$

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(6) P. Waentig, *Z. physik. Chem*, **68**, 513 (1909).

(7) J. H. Hildebrand, *Phys. Rev.*, **34**, 984 (1929).

(8) G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).

The constant, A, is calculated from the "cohesive energy densities," $\Delta E/V = a$ of the pure components, by the relation

$$A = (\sqrt{a_1} - \sqrt{a_2})^2 \tag{7}$$

The following values of a, as cal. per cc., at 25°, were used for the substances here concerned: $TiCl_4$, 76.0; CCl_4, 73.0; $C_2H_4Br_2$, 97.5; CS_2, 100.0; $SiCl_4$, 58.0; I_2, 192. These values were taken, in part, from a paper by the senior author;[7] the others were calculated from the vapor pressure curves and the molal volumes.

It can be seen from Table II that the values of A calculated from the solubility data vary with temperature more than the values of k, except in the case of dibromoethane. This variation would probably be largely avoided by treating A, not as a constant, as implied in Scatchard's treatment, but as a variable, since $\Delta E/V$ decreases with temperature. Since $V\Delta E = a$, the van der Waals constant, with sufficient accuracy for this purpose, it would be preferable to substitute for Equation 7 the expression

$$A = \left(\frac{\sqrt{a_1}}{V_1} - \frac{\sqrt{a_2}}{V_2}\right)^2 \tag{8}$$

In Fig. 2 are included several solubility curves in addition to those previously published. Stannic iodide, as has been pointed out in our paper on its solubilities, gives ideal solutions with iodine. Solutions of iodine in *p*-dinitrobenzene are interesting as illustrating, first, limited solubility in the liquid state, second, the irregular temperature coefficient of a brown solution. The dotted curves in Fig. 2 indicate brown solutions, and it is very evident that they do not belong to the family of violet solutions. In the case of carbon disulfide, the dotted line is drawn in the direction of some rather inaccurate values at much lower temperatures. The color does not change very much as the temperature is lowered, but the absorption band undergoes a great change.

Summary

The solubility of iodine in ethylene bromide and in silicon and titanium tetrachlorides has been measured over a wide range of temperature. The "regularity" of iodine solutions is discussed, together with the relation between solubility and internal pressure and the applicability of an equation derived by Scatchard.

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Inhibitors in the Decomposition of Hydrogen Peroxide by Catalase

BY HUBERT N. ALYEA AND JAMES PACE*

In a recent paper Jeu and Alyea[1] found that nineteen different substances have the same inhibitory powers for the autoxidation of sodium sulfite as for the photo-polymerization of vinyl acetate in a hydrogen atmosphere. On the other hand, entirely different inhibitory powers were obtained in studying the photolysis of hydrogen peroxide at 75°. These latter data suggested a useful method for investigating the much-discussed[2] mechanism of the decomposition of hydrogen peroxide by catalase. If the inhibitory powers are the same whether the decomposition is accelerated by catalase or by light, it would be obvious that the reaction chains were being initiated at the surface of the catalase and extending out into the reaction medium in much the same way as the hydrogen–oxygen explosion extends out from the walls of the containing vessel.[3] This work was carried out, then, to decide whether the decomposition occurs at the surface of the catalase or whether the catalase merely initiates chains.

Experimental

Catalase.—Freshest sheep's liver was minced, digested with water and filtered through cheesecloth. The catalase was precipitated from the filtrate by an equal volume of ethyl alcohol, filtered, redissolved in water, and the cycle repeated twice. The final dried precipitate, weighing about 0.5 g., was dissolved in 250 cc. of distilled water, protected from bacteria with a few drops of toluene, and stored in an ice-box. By diluting this solution 30,000 times, a stock catalase solution was prepared which gave measurable rates of decomposition for the hydrogen peroxide. It was stored in ice, and any deactivation of the solution, which amounted to about 10% per month, was made up by the addition of a few drops of the concentrated solution.

Inhibitors.—Merck C. P. products, without further purification, were dissolved in distilled water and stored in Pyrex bottles.

Hydrogen Peroxide.—Merck Superoxol was dissolved in sodium potassium hydrogen phosphate buffer and stored in a Pyrex flask. Decomposition of the peroxide from day to day was compensated for by adding a few drops of Superoxol. The concentration was so adjusted that at the beginning of the run there was 0.05 *M* buffer, *P*H 6.80, and 0.05 *M* hydrogen peroxide.

A new Pyrex test-tube was used for each run: 15 cc. of peroxide buffer was run in, followed by a total of 5 cc. of varying ratios of water–inhibitor solutions. The tube was then placed in the bath at 24.0 ± 0.1°, 5 cc. of catalase solution added, the solutions mixed, and a 5-cc. sample immediately titrated with approximately 0.01 *N* potassium permanganate. At five-minute intervals 5-cc. samples were removed and analyzed.

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* Commonwealth Fund Fellow.

(1) Jeu and Alyea, THIS JOURNAL, **55**, 575 (1933).

(2) Haldane, *Nature*, **130**, 61 (1932); *Proc. Roy. Soc.* (London), **B108**, 559 (1931); Richter, *Nature*, **129**, 870 (1932); Haber and Willstätter, *Ber.*, **64**, 2844 (1931); Kenner, *Ber.*, **65**, 705 (1932); and others.

(3) Alyea, THIS JOURNAL, **53**, 1324 (1931).

Results

Unfortunately the velocity constants are somewhere between unimolecular and bimolecular. Thus the unimolecular constants of 0.0628, 0.0566, 0.0486 for the first run in Table I are not nearly as satisfactory as the corresponding bimolecular values 0.00315, 0.00322, 0.00303; whereas other uninhibited runs often gave more satisfactory unimolecular than bimolecular constants. To obviate this difficulty, the following device was employed. The dropping values of the unimolecular constants were plotted as in Fig. 1, and the value at the time of mixing ($t = -0.5$) was taken as the true velocity constant. It must be emphasized why this removes the difficulty of deciding which constant to employ. The limiting value of the bimolecular constant $x/a(a - x)$ is x/a^2, while the unimolecular constant $\ln a/a - x$ in the approximate form $(x/a - x) + {}^1/_2(x/a - x)^2$ becomes x/a at vanishingly small values of x. In this paper it is not the absolute velocity constants but rather the *ratios* of these constants which are employed in calculating inhibitory powers. Therefore since a is the same for all runs, the same inhibitory powers will be obtained whether we compare x/a^2 or x/a.

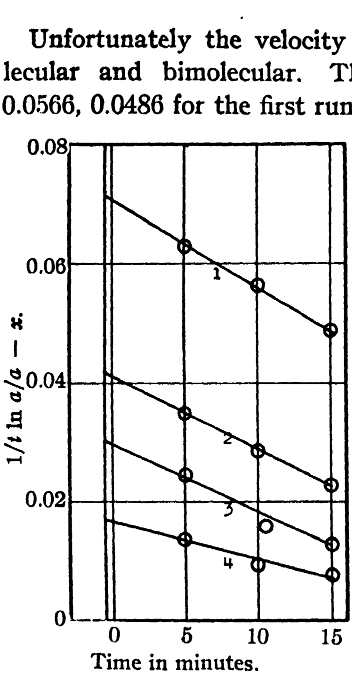

Fig. 1.—Moles peroxide: moles hydroquinone: Curve 1, ∞; Curve 2, 1250; Curve 3, 625; Curve 4, 250.

Catalase Concentration.—Using extrapolated unimolecular constants it was found that the rate of hydrogen peroxide decomposition was proportional to the concentration of the catalase, since peroxide solutions containing 0.1, 1, 5 and 10 cc. of catalase gave constants of 0.0017, 0.0143, 0.0720 and 0.1450, respectively.

Inhibitory Powers.—The effect of inhibitors is expressed satisfactorily by

$$1/t \ln (a/(a - x)) = K/(k_2 + kC) \quad (1)$$

where a is the initial permanganate titer, $a - x$ the titer at time t, K represents the factor initiating and continuing chains, and $k_2 + kC$ represents the chain breaking by a constant source k_2 and by the added inhibitor of concentration C and inhibitory power k. The significance of this equation is discussed fully in an earlier communication[1] along with the details for calculating the inhibitory powers k, and need not be repeated here. It suffices to state that from the plot of $C/t \ln a/a - x$ against $1/t \ln a/a - x$, the intercepts at the ordinate will give values inversely proportional to

TABLE I

DECOMPOSITION OF HYDROGEN PEROXIDE BY CATALASE INHIBITED BY HYDROQUINONE

Moles peroxide / Moles inhibitor	Time, minutes	Permanganate titer in cc. $(a - x)$	$1/t \ln a/a - x$ $\times 10^4$	Moles peroxide / Moles inhibitor	Time, minutes	Permanganate titer in cc. $(a - x)$	$1/t \ln a/a - x$ $\times 10^4$
∞	−0.5	..	(720)	625	−0.5	..	(300)
	0	23.6	...		0	24.2	...
	5	17.2	628		5	21.4	244
	10	13.4	566		10.5	20.5	158
	15	11.4	486		15	19.9	129
1250	−0.5	..	(417)	250	−0.5	..	(170)
	0	23.6	...		0	24.8	...
	5	19.8	347		5	23.2	136
	10	17.8	285		10	22.6	94
	15	16.8	226		15	22.2	76

the inhibitory power, *k*. Such a plot has been made for hydroquinone in Fig. 2, using the values in Table I. The values of the curve at the intercepts appear in Table II. Exactly the same was done for the other inhibitors, and the summary of intercepts for all of them is in Table II.

TABLE II

RELATIVE INHIBITORY POWERS

Inhibitor	$1/C$ range	Ordinate $\times 10^4$	Abscissa $\times 10^4$	Corrected ordinate[a] $\times 10^4$	Inhibitory powers (±15%) Catalase 24°	Inhibitory powers (±15%) Photolysis 75°
Pyrogallol	625–2500	0.817	829	0.681	3200[b]	3200[b]
Hydroquinone	250–1250	.870	685	.875	2500	8400
Catechol	625–2500	1.38	736	1.24	1750	8200
Resorcinol	125–250	1.54	789	1.35	1600	11000
p-Cresol	250–2500	2.74	626	3.03	720	5600
Phenol	25–250	13.8	690	13.8	160	11000
Propionic acid	2.5–15.5	19.6	711	19.1	110	640
Acetoxime	25–250	23.0	850	18.7	100[c]	1080
Methyl oxalate	25–250	37.8	633	41.6	50[c]	2000
Ethylamine	2.5–25	48.4	690	48.4	45[c]	20000
Benzylamine	6.25–25	62.0	690	62.1	35[c]	12000
Cocaine hydrochloride	25–250	143	656	150	14.5[c]	12000
Chloral hydrate	0.25-2.5	1430	691	1450	1.5[c]	790
Allyl alcohol	10.4–104	...	...	...	<1	150
Benzoic acid	25–250	...	...	...	<1[c]	9800
Benzyl alcohol	5	...	...	...	<1	6700
Ethyl alcohol	2.5–0.25	...	...	...	<1	130
Pyridine	0.25–0.625	...	...	...	<1	1040
Veronal	5–50	...	...	...	<1	1230

[a] Corrected abscissa taken as 0.0690. [b] Taken as standard. [c] May have deactivated the catalase, see Table III.

It is the result of runs at at least three different concentrations of each inhibitor. Simultaneous runs with a given inhibitor all fall along the same line, as in Fig. 2, but runs made at different times differ slightly due to irreproducibility of catalase activity and other factors. This variation is evidenced by the variation of the intercept at the abscissa in the fourth column of Table II. It is corrected for by taking the abscissa as 0.0690, and using for the ordinate the corrected value of 0.069 uncorrected ordinate/uncorrected abscissa. From the corrected value of the ordinate the relative inhibitory powers can be calculated by taking pyrogallol as the standard (k = 3200) as previously explained.[1] The inhibitory powers, so calculated, are given in the sixth column of Table II, and for reference the seventh column states the inhibitory powers previously found for the photolysis at 75°.

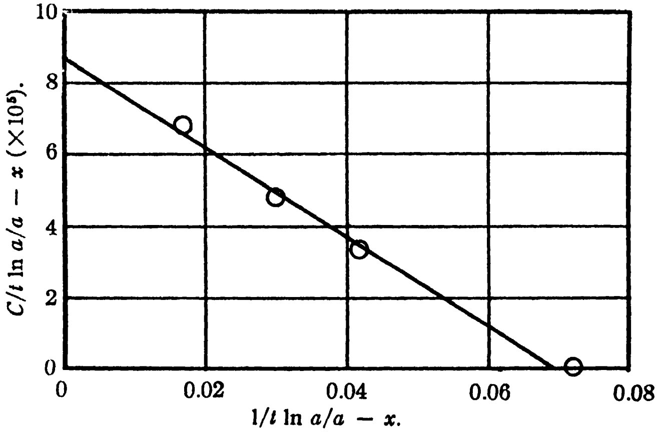

Fig. 2.

Pre-mixing Catalase and Inhibitor.—Another series of experiments was carried out in which 5 cc. of catalase was mixed with 5 cc. of inhibitor

TABLE III

EFFECT OF PRE-MIXING INHIBITOR WITH CATALASE

Inhibitor	Moles peroxide / Moles inhibitor	$1/t \ln a/a - x$		Inhibitor	Moles peroxide / Moles inhibitor	$1/t \ln a/a - x$	
		Pre-mixed × 10^4	Not pre-mixed × 10^4			Pre-mixed × 10^4	Not pre-mixed × 10^4
Allyl alcohol	26	670	690	Acetoxime	25	115	324
Benzyl alcohol	5	650	666		25	70	276
Catechol	250	210	219	Benzoic acid	250	480	690
p-Cresol	250	410	368	Benzylamine	2.5	805	138
Ethyl alcohol	0.25	680	690	Cocaine hydrochloride	25	300	506
Hydroquinone	625	255	294	Chloral hydrate	0.25	0	248
Phenol	62.5	355	345	Ethylamine	6.25	130	200
Propionic acid	6.25	092	099	Methyl oxalate	250	460	666
Pyridine	0.625	715	828				
Pyrogallol	250	92	81				
Resorcinol	125	150	168				
Veronal	5	690	721				

and allowed to stand for twenty minutes at room temperature. At the end of this time 15 cc. of the buffered peroxide solution was added and the run carried through in the usual way. The velocity constants obtained under these conditions are given in Table III. For comparison, constants obtained at the same inhibitor concentration but in which inhibitor, peroxide and catalase were added simultaneously are given in the last column.

Discussion

From Table II it appears that there is no parallelism between inhibitory powers in the reactions accelerated by light and by catalase.[4] The most serious objections to this comparison lie in the fact that the photolysis was carried out at 75° while the catalase reaction is carried out at 24°, and that we know from semi-quantitative experiments on inhibition of the thermal decomposition of hydrogen peroxide that certain of the substances do not inhibit thermolysis and photolysis to the same extent. To correct this, measurements are now in progress at Princeton to compare inhibitory powers for the peroxide decomposition accelerated by various inorganic catalysts as well as by catalase.

It will be noticed that we used buffer in the catalase reaction. The agreement with Equation 1 in which buffer was always present to the same concentration but the inhibitory concentration varied, favors the view that the former did not exert any inhibition. The photolysis experiments were not buffered, the inhibitor concentrations being so low that inhibition was never interpreted as due to change in P_H.

The many separate runs in Table III are not as reproducible as those in Table II, but they afford decisive evidence that catalase is not deactivated by standing at room temperature for twenty minutes with any of the first twelve inhibitors in the table. For if it were, we should anticipate increased inhibition upon standing, and the values in the third column would be lower than those in the fourth column. Doubt exists, however, about the seven inhibitors at the bottom of the table where the rate is slower

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[4] This is in disagreement with the conclusions drawn by Schwab, Rosenfeld and Rudolph [*Ber.*, **66**, 661 (1933)] in a recent paper which appeared shortly before the completion of this work. They conclude there is a possible parallelism. Unfortunately they had data for only four inhibitors, two of which did not substantiate parallelism. Ethyl and benzyl alcohols had inhibitory powers of < 0.5 and 1.4, respectively, for decomposition by catalase as contrasted with 130 and 6700 for the photolysis. There are two other corrections to be pointed out. Their second table of inhibitors in various types of reactions consists of six columns of our data and two columns of their own. Their error was in choosing hydroquinone as a standard, particularly in the three columns of sulfite oxidation. For Table X, Jeu and Alyea show that hydroquinone has abnormal inhibition in the sulfite reaction, perhaps due to the formation of a hydroquinone sulfonate. [Alyea and Bäckström, THIS JOURNAL, **51**, 90(1929).] This is why we have always chosen pyrogallol rather than hydroquinone as a standard throughout our work. Second, the use of Equation 1 is urged in calculating inhibitory powers. It is inadvisable to use as a measure of inhibitory powers the reciprocal of the concentration at which equal inhibition occurs, for this holds only when kC is so large that k_1 is negligible, whereby kC becomes inversely proportional to the reaction rate. Now $k_1 = kC$ at 50% reduction in rate. Therefore, under conditions of their paper, which was only 20% reduction in rate, they could calculate only approximate inhibitory powers by this method; whereas with their excellent experimental data very exact inhibitory powers could have been calculated by use of Equation 1.

when the inhibitor is mixed with the catalase twenty minutes before adding the peroxide. Unfortunately these data do not exclude the possibility of the inhibitor deactivating a catalase–peroxide complex, although agreement with Equation 1 rather disparages such a view.

The value of k_2 *may be used in calculating minimum chain length according to the method of Jeu and Alyea, to which the reader is referred for details.* k_2 *is given from the data for pyrogallol in Table II as* $3200 \times 0.0000681/0.0690 = 3.16$. *The chain length is* $6400/k_2 = 2000$. This should be compared with the value of 2000 from the photolysis at 75°.

We wish to thank Mr. J. L. Osmer for preparing the catalase with which this work was carried out.

Summary

1. The decomposition of hydrogen peroxide by catalase has been inhibited by nineteen organic substances.

2. Their inhibitory powers differ markedly from the inhibitory powers previously found for the same substances in the photolysis of hydrogen peroxide at 75°.

3. With twelve of the nineteen inhibitors, allowing a catalase–inhibitor mixture to stand some time before adding peroxide gave the same inhibitory powers as runs in which inhibitor, peroxide and catalase were mixed simultaneously. This is interpreted to mean that the inhibitor did not deactivate the catalase. The remaining seven inhibitors, however, appeared to deactivate the catalase somewhat.

4. The value of minimum chain length, calculated from k_2 in the equation $1/t \ln a/a - x = K/(k_2 + kC)$ according to the method of Jeu and Alyea is 2000.

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The Conversion of Ammonium Cyanate into Urea. Mechanism and Kinetic Salt Effect

BY J. C. WARNER AND FRED B. STITT

Studies of the rate of conversion of ammonium cyanate into urea have been the subject of a number of investigations.[1] In these investigations there is agreement upon the following points. (a) The reaction is bimolecular in character. (b) The reaction is not complete in aqueous solution, some unchanged NH_4OCN remaining at equilibrium. (c) There is a slight side reaction leading to the formation of carbonate. (d) The bimolecular rate constant increases with a decrease in the concentration of NH_4OCN. (e) The rate constant is higher in mixtures of water with alcohols, sugars, acetone, etc., than it is in pure water.

Concerning the exact nature of the bimolecular mechanism, there has been considerable controversy. J. Walker and Hambly, J. Walker and Kay, and Ross[1] supported the assumption that the rate depends upon collisions between ammonium ions and cyanate ions (ionic mechanism). Chattaway[2] argued against the ionic mechanism and assumed the rate to depend upon collisions between molecules of ammonia and isocyanic acid. This view, in a modified form, was supported by Werner,[3] and E. E. Walker[1] favored a non-ionic mechanism. Recently, Moelwyn-Hughes[4] has assumed the rate to depend upon collisions between unionized molecules of ammonium cyanate. Contrary to the results of earlier investigators, Doyle[5] reported the rate constants at 35 and 55° to be practically independent of the ammonium cyanate concentration. Since the magnitude of the kinetic salt effect can be used to decide the mechanism of the reaction, a systematic investigation of the effect of the concentration of NH_4OCN and added salts upon the velocity of the conversion was undertaken.

According to the Brönsted theory,[6] if the rate depends upon collisions between NH_3 and HOCN molecules or between two molecules of undissociated NH_4OCN, there should be only a small positive or negative primary salt effect and the effect should be a linear function of the ionic strength. If, however, the rate depends upon collisions between ammonium and cyanate ions, the primary salt effect should be negative and a function of the square root of the ionic strength. This was the type of salt effect indicated in the preliminary results obtained by Mr. J. S. Peake.[7]

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(1) J. Walker and Hambly, *J. Chem. Soc.*, **67**, 746 (1895); J. Walker and Kay, *ibid.*, **71**, 489 (1897); Ross, *ibid.*, **105**, 690 (1914); E. E. Walker, *Proc. Roy. Soc.* (London), **A87**, 539 (1912).

(2) Chattaway, *J. Chem. Soc.*, **101**, 170 (1912).

(3) Werner, *ibid.*, **103**, 1010 (1913).

(4) Moelwyn-Hughes, *Chem. Rev.*, **10**, 244 (1932).

(5) Doyle, Thesis, Liverpool, 1922; reviewed by Moelwyn-Hughes, Ref. 4.

(6) Brönsted, *Chem. Rev.*, **5**, 231 (1928); La Mer, *ibid.*, **10**, 179 (1932).

(7) J. S. Peake, Thesis, Carnegie Institute of Technology, 1932.

Materials and Experimental Procedure.—Silver cyanate was prepared by heating a solution containing C. P. silver nitrate and about five equivalents of Eastman "Highest Purity" urea. The silver cyanate was filtered off from time to time, carefully washed and then dried in a vacuum desiccator. Solutions of C. P. ammonium chloride and potassium thiocyanate were standardized by precipitating the silver salts and weighing. All experiments were carried out at 70 ± 0.05°. The ammonium cyanate solutions were prepared by agitating standard ammonium chloride solution with a slight excess of silver cyanate until the solution was free of chloride ion. The precipitated silver chloride was filtered off and the solution, in the reaction flask, heated in an open flame to approximately the thermostat temperature. As soon as the solution reached the thermostat temperature, an initial sample was pipetted from the reaction flask into an excess of standard silver nitrate solution. The precipitated silver cyanate was filtered off and an aliquot portion of the filtrate, made acid with nitric acid, was titrated with standard potassium thiocyanate, using concentrated ferric nitrate as an indicator. As the reaction proceeded other samples were treated in a similar manner. In experiments with added salts, a weighed amount of the C. P. salt was dissolved in the freshly prepared ammonium cyanate solution.

The titration of an aliquot portion of the filtrate eliminates washing the silver cyanate (which is appreciably soluble) and allows a convenient volume to be used in all titrations. In all runs, concentrations of silver nitrate and potassium thiocyanate solutions were chosen so that (a) a considerable excess of silver nitrate was present to ensure more complete precipitation of the silver cyanate, (b) the back titrations changed considerably during the course of a run, (c) errors in titration and pipetting were relatively unimportant.

Experimental Results.—In the calculation of velocity constants from our data, we have considered the effect of the back reaction, the side reaction leading to carbonate formation, and the changing ionic strength during the course of the reaction. The effect of the back reaction is easily less than our experimental error up to 70% conversion. This is evident from an examination of the data in columns 6 and 7 in Table II. The effect of carbonate formation is also less than the experimental error. Not enough carbonate has formed at 70% conversion to give a precipitate with calcium nitrate even when the initial concentration of ammonium cyanate is 0.5 mole per liter. If the reaction were strictly bimolecular, the reciprocal of the ammonium cyanate concentration should be a linear function of the time. We have therefore plotted $1/(NH_4OCN)$ against t (min.) and assumed a linear relationship over such a range as seemed justified by the experimental points. In this way the second-order constant for the mean ionic strength of the range was calculated. The results obtained in this manner are listed in Table I.

In Fig. 1, log k is plotted against the square root of the ionic strength. It was very difficult to obtain reliable experimental results in the range $\sqrt{\mu} = 0$ to 0.1 due to the difficulty of simultaneously meeting all three conditions noted under procedure. When much excess silver nitrate is used, the titrations become inaccurate, whereas for small excesses, appreciable amounts of AgOCN remain in solution. The effect of dissolved AgOCN is to give values of the velocity constant which are too high.

TABLE I

Run	Initial molality NH_4OCN	Range μ used in calcns.	Midpoint of range (μ)	$\sqrt{\mu}$	Bi-molecular k (min.)	Minus log k	Molality added salt
Pure NH_4OCN (no added salt)							
36	0.01	0.0077-0.0065	0.00709	0.0843	0.505	0.297	
15	.025	.020- .013	.0165	.1285	.427	.369	
30	.05	.028- .0078	.0182	.135	.465	.332	
31	.05	.023- .0135	.0183	.135	.433	.367	
35	.025	.023- .017	.0200	.141	.447	.350	
33	.20	.029- .019	.0243	.156	.428	.368	
37	.10	.026- .022	.0244	.156	.415	.388	
17	.05	.038- .023	.0306	.175	.379	.421	
31	.05	.046- .023	.0346	.186	.394	.404	
33	.20	.044- .029	.0366	.191	.392	.406	
30	.05	.046- .029	.0370	.192	.376	.424	
22	.10	.070- .043	.0567	.238	.357	.447	
21	.10	.069- .051	.0597	.244	.345	.462	
28	.10	.084- .041	.0628	.251	.354	.451	
37	.10	.089- .060	.0745	.272	.341	.467	
33	.20	.170- .078	.124	.352	.301	.521	
34	.35	.281- .108	.196	.443	.283	.548	
32	.50	.407- .097	.252	.502	.262	.582	
KNO_3 as added salt							
20	0.05	0.063-0.044	0.0533	0.231	0.380	0.420	0.025
46	.05	.095- .076	.0857	.293	.345	.462	.05
19	.05	.094- .084	.089	.298	.338	.471	.05
18	.05	.138- .119	.129	.359	.319	.496	.10
13	.10	.194- .138	.164	.405	.295	.530	.10
45	.10	.190- .144	.167	.409	.294	.532	.10
16	.05	.245- .231	.238	.488	.288	.540	.20
44	.10	.265- .245	.255	.505	.267	.573	.20
43	.10	.385- .344	.365	.604	.247	.607	.30
42	.10	.488- .434	.461	.659	.241	.618	.40
NaF as added salt							
24	0.05	0.144-0.115	0.129	0.359	0.309	0.510	0.10
49	.10	.169- .131	.150	.387	.297	.527	.10
23	.04	.209- .195	.202	.449	.272	.565	.17
48	.10	.388- .341	.365	.604	.234	.630	.30
47	.10	.489- .456	.473	.679	.223	.651	.40

Discussion of Results

From Fig. 1 it is evident that the velocity constants at various ionic strengths, with or without added salts, determine a fairly smooth curve. In general, the velocity constants, at equal ionic strengths, are somewhat smaller in the presence of sodium fluoride and somewhat higher with potassium nitrate, than they are for pure ammonium cyanate. By extrapolation to $\sqrt{\mu} = 0$, a value $k_0 = 0.615$ is obtained. This value represents the velocity constant at 70°, free from all salt effects. Due to the difficulty in obtaining reliable results at low ionic strengths, we have been guided in our extrapolation by the theoretical limiting slope indicated by the Brönsted theory

$$\log k = \log k_0 + \log (\gamma_{NH_4^+}\gamma_{OCN^-}/\gamma^\circ_X)$$
$$= \log k_0 - (2 \times 1.816 \times 10^6 \sqrt{\mu})/(DT)^{3/2}$$

Using Wyman's[8] value of 63.5 for the dielectric constant of water at 70°, we obtain

$$\log k = \log k_0 - 1.13\sqrt{\mu}$$

This limiting slope is shown by the dotted line in Fig. 1.

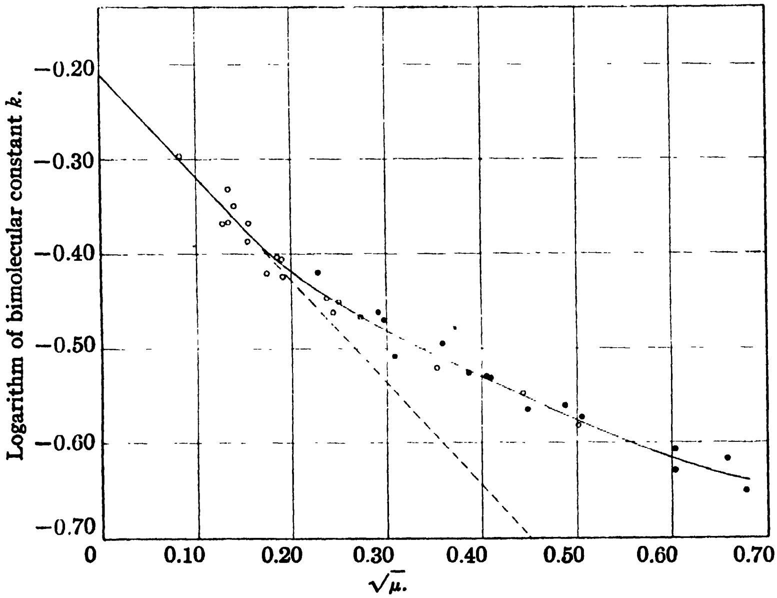

Fig. 1.—⊙, No added salt; ●, KNO_3 as added salt; ⊗, NaF as added salt.

The Limiting Velocity Constant.—We have considered the possibility of calculating the limiting velocity constant (k_0) directly from experimental data by taking into account the effect of the changing ionic strength during the course of the reaction. According to the Brönsted theory, the rate of formation of urea is given by the expression

$$dx/dt = k_1 C_{NH_4^+} C_{OCN^-} (\gamma_{NH_4^+}\gamma_{OCN^-}/\gamma^\circ_X) - k_2 C_{urea}$$

Let a = initial concentration of ammonium cyanate, b = initial concentration of urea and assume $\gamma_{NH_4^+} = \gamma_{OCN^-}$ and that $\gamma^\circ_X = 1$. Substitute $k_2 = k_1K_e$, where $K_e = 1.62 \times 10^{-4}$ is the thermodynamic equilibrium constant at 70°.[9] Our velocity equation then becomes

$$\int k\,dt = \int \frac{dx}{(a-x)^2\gamma^2_\pm - K_e(b+x)}$$

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(8) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(9) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 587.

When γ is expressed as a function of the ionic strength, an expression is obtained which we have been unable to integrate analytically. It may, however, be integrated graphically if $\gamma_{\pm}$ is known as a function of the ionic strength. No data are available on the activity coefficients of NH_4OCN, but we have applied this method to the data obtained in a number of our experiments, using the activity coefficients of ammonium nitrate at 0°.[10] The results of a typical calculation are given in Table II. A summary of the results for a number of runs is given in Table III. Since the combined effect, on the activity coefficients, of an increase in temperature and a decrease in dielectric constant in going from 0 to 70° is probably smaller than the error involved in the assumption of equal activity coefficients for NH_4OCN and NH_4NO_3, no correction was thought necessary for our purpose.

TABLE II

Run 31. Initial molality of NH_4OCN, 0.05. No added salt

Time, min.	Molality NH_4OCN	Molality urea	Δ(Urea)	$\gamma_{NH_4NO_3}$	$\gamma^2(NH_4OCN)^2$	K_e(Urea)	$1/[\gamma^2(NH_4OCN)^2 - K_e(Urea)]$	Area from $t = 0$	Limiting k
0	0.04575	0.00425		0.789	130.3×10^{-5}	0.1×10^{-5}	767		
			0.00725						
10	.03850	.01150		.803	95.6	.2	1048	6.56	0.656
			.00462						
20	.03388	.01612		.810	75.3	.3	1332	12.04	.602
			.00601						
35	.02782	.02213		.825	52.7	.4	1911	21.68	.620
			.00489						
55	.02298	.02702		.836	36.9	.4	2740	32.98	.600
			.00526						
85	.01772	.03228		.853	22.85	.52	4480	51.9	.611
			.00417						
125	.01355	.03645		.868	13.85	.59	7540	76.7	.614
			.00335						
175	.01020	.03980		.883	8.11	.65	11820	108.5	.620

TABLE III

Run	Initial molality NH_4OCN	Initial molality added salt	Salt added	Mean limiting k	Run	Initial molality NH_4OCN	Initial molality added salt	Salt added	Mean limiting k
30	0.05		None	0.60	49	0.10	0.10	NaF	0.61
31	.05		None	.61	48	.10	.30	NaF	.66
17	.05		None	.61	47	.10	.40	NaF	.70
11	.05		None	.61	19	.05	.05	KNO_3	.59
28	.10		None	.62	20	.05	.025	KNO_3	.62
37	.10		None	.60	18	.05	.10	KNO_3	.66
7	.10		None	.61	16	.05	.20	KNO_3	.69
12	.10		None	.60	13	.10	.10	KNO_3	.66
33	.20		None	.60	45	.10	.10	KNO_3	.65
34	.35		None	.74 down	44	.10	.20	KNO_3	.68
32	.50		None	.77 down	43	.10	.30	KNO_3	.72
23	.043	0.17	NaF	.63	42	.10	.40	KNO_3	.77

The values of the limiting k thus found show little variation over the range of ionic strength at which the assumption of equal activity coefficients for NH_4OCN and NH_4NO_3 seems valid. The close agreement between the mean velocity constant calculated by this method and the extrapolated value from Fig. 1 should be noted. Above $\mu = 0.1$, the value of the limiting constant increases with increasing ionic strength showing that the activity coefficient of NH_4OCN decreases less rapidly than that of

(10) Scatchard and Prentiss, THIS JOURNAL, 54, 2702 (1932).

NH_4NO_3 with increase of ionic strength. In those runs with no added salt in which the initial concentration of NH_4OCN was high, the limiting constant drops from a high value toward the extrapolated value as the reaction proceeds. The results obtained by this method suggest the important possibility of determining activity coefficients from velocity measurements when the reaction can be followed with extreme accuracy. This method should be particularly useful in solvent mixtures where the usual methods are less applicable. One should, however, take into account La Mer's[11] suggestion that the activity coefficients entering into rate equations are probably not always the true thermodynamic coefficients.

Inasmuch as we have observed a marked negative primary salt effect of the magnitude predicted by the Brönsted theory for a reaction between univalent ions of opposite charge, our data strongly support the assumption of Walker and Hambly that the rate of conversion of ammonium cyanate into urea depends upon collisions between ammonium and cyanate ions. Investigations now in progress in this Laboratory on the effect of the dielectric constant of the solvent upon the rate of this reaction also strongly support the ionic mechanism.

Summary

1. The dependence of the rate of conversion of ammonium cyanate into urea upon ionic strength has been determined in the presence and absence of added salts.

2. A negative primary salt effect of the magnitude predicted by the Brönsted theory has been observed.

3. The observed salt effects support the assumption that the rate of conversion of ammonium cyanate into urea depends upon collisions between ammonium and cyanate ions, and not upon collisions between undissociated molecules of ammonium cyanate as has been suggested recently.

4. A method is presented for evaluating the limiting velocity constant (free from salt effects) directly from the experimental data when activity coefficients are known. The constant calculated by this method is in good agreement with that obtained by extrapolating the ordinary bimolecular constant to zero ionic strength.

5. The possibility of determining activity coefficients from velocity measurements is suggested.

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[11] La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Preparation and the Quaternary Ammonium Decomposition of Formocholine

BY T. D. STEWART AND H. P. KUNG

Formocholine chloride, $(CH_3)_3NCH_2OH^+Cl^-$, is interesting as a quaternary ammonium compound since a hydrogen attached to an atom in the β position to the nitrogen should be to some extent ionized. According to the theory[1] of quaternary ammonium decompositions such an ionization should result in the reaction

$$(CH_3)_3N^+—CH_2OH \overset{A}{\rightleftarrows} (CH_3)_3N^+—CH_2O^- + H^+ \xrightarrow{B} (CH_3)_3NH^+ + CH_2O \quad (1)$$

This is analogous to the reaction

$$(CH_3)_3N^+—CH_2—CH_2—C_6H_5 + OH^- \longrightarrow (CH_3)_3N + C_6H_5CH{=}CH_2 + H_2O \quad (2)$$

which takes place with unusual ease, due to the activation of the β hydrogen by the phenyl group. In these reactions three situations may occur: (1) the decomposition is preceded by a relatively rapid ionization, as in Equation (1); (2) the decomposition proceeds only in the presence of highly basic ions, such as hydroxide ion, and then by a path whose rate is dependent upon the number of collisions of the two ions (Equation (2)); and (3) the reaction rate is independent of the hydroxide ion concentration and first order in the quaternary ion concentration, suggesting that the rate determining step is the rate of ionization (or rate of activation) of the quaternary ion. Evidence for this was looked for by Stewart and Korpi[2] among the α-amino nitrile derivatives, $R_3NCH_2CN^+OH^-$. Hughes and Ingold[3] report facts regarding the decomposition of the ion $(CH_3)_3N^+$-$CH(C_6H_5)_2$ which they interpret in this way. Formocholine belongs to the case (1), a rapid reversible ionization followed by the decomposition of the neutral residue as the rate determining step.

The Preparation of Formocholine Chloride.—The preparation has been reported by various authors, whose methods have failed in our hands.

Hofmann[4] and later Schmidt and Litterschied[5] heated a mixture of silver oxide and iodomethyltrimethylammonium iodide for several days, and isolated gold and platinum double salts, presumably of formocholine chloride.

$$(CH_3)_3N^+—CH_2I + AgOH \longrightarrow (CH_3)_3N^+—CH_2OH + AgI \quad (3)$$

The yield was apparently small, and in view of the extremely rapid decomposition of formocholine in alkali, as described below, we feel safe in saying that their product was not formocholine. It could have been the ether, $[(CH_3)_3N—CH_2—O—CH_2—N$-

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[1] (a) v. Braun, *Ann.*, **382**, 1 (1911); (b) Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., Inc., New York, 1923, p. 135; (c) Stewart and Aston, THIS JOURNAL, **49**, 1720 (1927); (d) Hanhart and Ingold, *J. Chem. Soc.*, 997 (1927).

[2] Stewart and Korpi, THIS JOURNAL, **54**, 3977 (1932).

[3] Hughes and Ingold, *J. Chem. Soc.*, 69 (1933).

[4] Hofmann, *Jahresb.*, 377 (1859).

[5] Schmidt and Litterschied, *Ann.*, **377**, 74 (1904).

$(CH_3)_3]^{++}Cl_2^-$, whose platinum double salt contains one molecule of water of crystallization. The platinum double salts of formocholine and of the above hydrated ether are described by Litterschied as decomposing at 230 and 232°, respectively; the true formocholine double salt decomposes sharply at 246° if the bath temperature is raised rapidly, otherwise the decomposition temperature is 252°, corresponding to that of the double salt of trimethylammonium chloride. The above ether does not decompose in boiling dilute alkali.

Renshaw and Ware[6] reported formocholine formed by the reactions

$$(CH_3)_3N + ClCH_2{-}O{-}CO{-}CH_3 \longrightarrow (CH_3)_3N^+{-}CH_2{-}O{-}CO{-}CH_3 + Cl^- \quad (4)$$

$$(CH_3)_3N^+{-}CH_2{-}O{-}CO{-}CH_3 + C_2H_5OH \xrightarrow[\text{Alc.}]{\text{Dil. HCl}} (CH_3)_3N^+{-}CH_2OH + CH_3{-}CO_2C_2H_5 \quad (5)$$

They heated the acetylformocholine with "very dilute" alcoholic hydrochloric acid at 56° for twenty-four hours. The only fractions of the product formed by their procedure which we have found to correspond to their chlorine analysis proved to be approximately equal molal mixtures of unchanged acetylformocholine chloride and trimethylammonium chloride. Moreover, the pure formocholine chloride decomposes completely in one hour at 40° in 0.03 *N* alcoholic hydrochloric acid, and in twenty-four hours at any low concentration of acid would be largely decomposed at 56°.

Experimental

The method of Renshaw and Ware has been modified.

Acetylformocholine Chloride.—Fifty-eight grams of chloromethyl acetate b. p. (60 mm.) 49° and 29 g. of trimethylamine in 68 g. of propyl alcohol stood for twenty hours in an ice-bath. The crystals which separated (55% yield) were almost pure acetylformocholine chloride; a second crop containing some trimethylamine hydrochloride was precipitated from the mother liquor with ether; total yield 72 g. Recrystallization from hot propyl alcohol gave the pure salt of the composition $(CH_3)_3NCH_2OCOCH_3Cl\cdot{}^1/_2H_2O$. Cl found, 20.3; calcd. 20.1. Drying in a vacuum desiccator over phosphorus pentoxide gave the pure anhydrous salt.

Bis-dimethylaminomethylether-bis-methyl chloride occurred as a by-product in the above preparation, due to the presence of dichloromethyl ether as an impurity in the chloromethyl acetate. It was isolated by treating the last fractions of the crude acetylformocholine with excess 0.1 *N* sodium hydroxide on the steam-bath until all the liberated trimethylamine had been driven off, acidifying with hydrochloric acid and evaporating to dryness. The salt was extracted from the sodium chloride with hot propyl alcohol and recrystallized. Equivalent weights (by chlorine analysis) 125.0 and 125.3, calculated for $[(CH_3)_3N{-}CH_2]_2O\cdot Cl_2\cdot H_2O$, 125.5. After four days in a vacuum desiccator over phosphorus pentoxide the equivalent weights found were 116.3 and 116.5.

Formocholine Chloride.[7]—Three grams of acetyl formocholine chloride was dis-

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[6] Renshaw and Ware, THIS JOURNAL, **47**, 2990 (1925).

[7] The only other acyclic salts of this structure known to us were prepared by Ingold and Rothstein [*J. Chem. Soc.*, 8 (1929)] by the reaction

$$CH_2Cl{-}CH{=}CH{-}N^+(CH_3)_3 \xrightarrow{+O^-C_2H_5} CH_2{=}CH{-}CH(OC_2H_5){-}N^+(CH_3)_3 \xrightarrow[\text{HCl}]{\text{concd.}} CH_2{=}CH{-}CH(OH)N^+(CH_3)_3$$

The α-hydroxyallyl derivative was ozonized in acetic acid, and the ozonide decomposed in boiling 30% acetic acid to yield $CHO{-}CH(OH){-}N^+(CH_3)_3$. Compared to formocholine, this is evidence of surprising stability. Similar attempts to hydrolyze the compound $CH_2(OR){-}N^+R_3$, derived from α-amino ethers [*cf.* Stewart and Aston, *loc. cit.*, and Robinson and Robinson, *J. Chem. Soc.*, **123**, 532 (1923)] resulted only in the corresponding tertiary amine salt.

solved in 50 cc. of 5 *N* hydrochloric acid, and the solution allowed to stand at room temperature until the hydrolysis was complete. In this experiment a larger amount of aqueous acid was used than necessary, which permitted the withdrawal of portions for analysis to determine the extent of the hydrolysis. The samples were diluted with ice-cooled water and the free acid neutralized by 0.1 *N* sodium hydroxide to the bromo thymol blue end-point. A known excess of standard alkali was then added to each, and the solution allowed to stand for one and a half hours at room temperature. The alkali was then back titrated and the amount of acetyl compound remaining in the sample calculated from the alkali consumed. The hydrolysis was practically complete within ten hours. The remaining stock solution was evaporated at room temperature *in vacuo* over soda lime and calcium chloride. The resulting sirup was taken up with 10 cc. of propyl alcohol, and the addition of ether brought down the salt as a viscous solution. To obtain the crystalline salt, the precipitate was dissolved in 20 cc. of butyl alcohol at 25-30°, and the solution cooled to ice temperature. The yield of this crop of salt was about 34% of the theoretical. Additional salt was recovered from the mother liquor by slow addition of ether, but was contaminated by trimethylamine hydrochloride.

Anal. Calcd. for $C_4H_{12}ONCl$: Cl, 28.23. Found: Cl (Volhard), 28.20, 28.23.

When dissolved in water, the salt decomposed very rapidly according to the equation

$$(CH_3)_3N^+CH_2OH + Cl^- = (CH_3)_3NH^+ + Cl^- + CH_2O \qquad (6)$$

The formaldehyde produced by this decomposition was determined by the bisulfite method; yield in two samples, 94.5 and 97.0%. Trimethylamine was determined by distilling a weighed sample with an excess of 0.1 *N* sodium hydroxide in a Kjeldahl apparatus; yield 98.7%.

The chloroplatinate of formocholine was made by dissolving the salt in absolute alcohol, and immediately precipitating with chloroplatinic acid. The orange-yellow precipitate was analyzed: calcd. for $(C_4H_{12}ON)_2PtCl_6$, Pt, 33.2; found, 32.9, 33.1. This chloroplatinate is very little soluble in alcohol. When dissolved in warm water, it decomposes to give a strong odor of formaldehyde. It decomposes sharply at 246° when it is heated very rapidly. This is accomplished by heating the bath to 245° before placing the melting point tube in it. Whenever the temperature was raised slowly, the chloroplatinate gave the decomposition temperature of 252°, which is the decomposition temperature of trimethylammonium chloroplatinate.[8]

The Hydrolysis and Alcoholysis of Acetylformocholine.—At *P*H 8.8 the hydrolysis is half complete in about seven minutes at room temperature, yielding trimethylamine, formaldehyde and acetate ion; in *N*/2 hydrochloric acid the hydrolysis is half complete in about nineteen hours at room temperature, as followed by the acetic acid produced; in water only 33% had hydrolyzed in ten days at room temperature. Alcoholysis, with the formation of ethyl acetate, trimethylamine and formaldehyde is catalyzed by both hydrogen chloride and trimethylamine. In concentrations of acid of the order *N*/10 the alcoholysis is very slow; mixtures of unchanged acetylformocholine with trimethylamine hydrochloride were obtained.

Decomposition of Formocholine Chloride in Slightly Acidified Alcoholic Solution.—0.32 g. of formocholine chloride was dissolved in 20 cc. of absolute alcohol; 10 cc. of the solution was run into an excess amount of chloroplatinic acid. Calcd. for $(C_4H_{12}ON)_2PtCl_6$, Pt, 33.2; found, 33.5. The other 10 cc. of the solution was acidified with 0.05 cc. of 5 *N* hydrochloric acid and heated at 40-50° for an hour. After the resulting solution had cooled to room temperature, it was precipitated with excess chloroplatinic acid. The analysis of the precipitate indicated trimethylammonium chloroplatinate: calcd. for $(C_3H_{10}N)_2PtCl_6$, Pt, 37.0; found, 37.1, 37.0. The compound would be more stable in more acidic solutions, but this was sufficient to show the difficulty of obtaining it through the slow alcoholysis of the acetyl derivative.

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[8] Two isomeric platinum complexes exist, one being mentioned in the introduction. The other is the double salt of the amine oxide derivative, $(CH_3)_3NOCH_3$ Cl. A sample was prepared and purified: Pt found, 32.9; calcd., 33.2. It decomposed sharply at 236° when put into the bath at 230° or above. When heated in water no odor of formaldehyde could be detected; the salt may be recrystallized from hot water.

Acetylation of Formocholine Iodide.—One and one-half grams (crude) was treated with about 15 cc. of acetic anhydride (in which it is not soluble) and allowed to stand at room temperature for two weeks with occasional shaking. During this time some long needle crystals separated from the brown solution. The solution was diluted with ether, filtered, and the product recrystallized once from hot propyl alcohol, yield 1.0 g.; decomposed at 150–152° (decomposition temperature of acetylformocholine iodide is 152°); I, calcd. for acetylformocholine iodide 49.0; calcd. for formocholine iodide 58.5; found, 51.0. Acetic acid produced by alkaline hydrolysis: calcd. for acetylformocholine iodide, 0.00386 mole/g.; found, 0.00341 mole/g. From the above two determinations it is calculated that the sample contains 85.0 mole per cent. of acetylformocholine iodide.

Triethyl-hydroxymethyl-ammonium Chloride.—This was prepared from triethylacetoxymethylammonium chloride, which was in turn prepared from chloromethyl acetate and triethylamine in equivalent amounts. The latter reaction requires two weeks at room temperature or about ten hours at 70°, and the product was identified as the chloroplatinate double salt: calcd. for $(C_9H_{20}NO_2)_2PtCl_6$, Pt, 25.8; found, 25.9, 25.6. No attempt was made to isolate the acetoxy compound; it was converted to the hydroxy compound through the same procedure used for formocholine chloride.

Anal. (Volhard) Calcd. for $C_7H_{18}NOCl$: Cl, 21.15. Found: 21.4.

This salt also decomposes rapidly when dissolved in water, and the formaldehyde produced in the process when determined by the bisulfite method was 95.5% of the theoretical amount.

The Decomposition of Formocholine and its Triethyl Homolog.—The decomposition was followed in buffered solutions through the change in the refractive index as measured by a Zeiss interferometer. This instrument cannot be used at temperatures far from room temperature.

Interferometer Measurements.—The reference solution was a mixture, in equal volumes, of the buffer salt solution and 0.3 *N* potassium chloride. The reacting solution was made up by diluting the same buffer solution with an equal volume of water and adding a measured amount of mixture, usually 10 cc., to about 0.09 g. of the formocholine chloride. The first reading could be taken within three minutes after preparing the solutions in the thermostat. The buffer solutions were made up as described by Sørensen,[9] of twice the desired concentration to allow for dilution as described above. The citrate solution contained 41.016 g. of citric acid and 400 cc. of 1.0 *N* sodium hydroxide, diluted to one liter; the hydrogen chloride solution was made up of 200 cc. of 1.0 *N* acid diluted to one liter. The *P*H value of the reacting solution with possible salt effect neglected was taken from Sørensen's tables. The small constant drift at the end of a run (Table I) was assumed to have also occurred throughout the run, and correction made for it.

To show that the interferometer readings were a measure of the reaction, the half-life at *P*H 1.418 was obtained colorimetrically with Schiff's reagent, using an empirical procedure. This was found to be 300 ± 15 minutes. Extrapolation of the curve in Fig. 1 to this *P*H value indicated a half-life of 285 minutes. Data for a typical experiment are given in Table I.

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(9) Clark, "The Determination of Hydrogen Ions" third ed., p. 209.

TABLE I

THE RATE OF DECOMPOSITION OF FORMOCHOLINE CHLORIDE AT CONSTANT HYDROGEN-ION CONCENTRATION

Expt. 6; P_H, 3.364. Temperature, 25.00 ± 0.02°; concn. 0.198 g. of formocholine chloride in 20 cc. of buffer solution

Time, t, minutes	Readings	Corr. readings (R_t)	$R_f - R_t$	Log ($R_f - R_t$)	Time, t, minutes	Readings	Corr. readings (R_t)	$R_f - R_t$	Log ($R_f - R_t$)
3	455	454.8	84.2	1.9253	13	530.0	527.3	9.8	0.9912
4	472	471.7	67.3	1.8280	14	532.0	531.1	7.9	.8976
5	484	483.7	55.3	1.7427	15	533.0	532.0	7.0	.8451
6	494	493.6	45.4	1.6580	18	536.5	535.2	3.8	.5798
7	503	502.5	36.5	1.5623	21	537.5	536.1	2.9	.4624
8	510	509.5	29.5	1.4698	24	540.0	538.4	0.6	
9	516.5	515.9	23.1	1.3636	30	541.0	539.0(R_f)		
10	520.0	519.4	19.6	1.2923	60	543.0	539.0		
11	524.0	523.3	15.7	1.1959	90	545.0	539.0		
12	527.5	526.7	12.3	1.0899					

Column three gives the readings of the instrument corrected for a small constant change due to unequal evaporation from the reference and reacting solutions. Column four gives the change in reading based upon the final corrected reading. This was shown to be proportional to the amount of reacting material present; when the logarithm of this quantity is plotted against the corresponding time, the points are found to lie on a straight line, indicating a rate law of the form

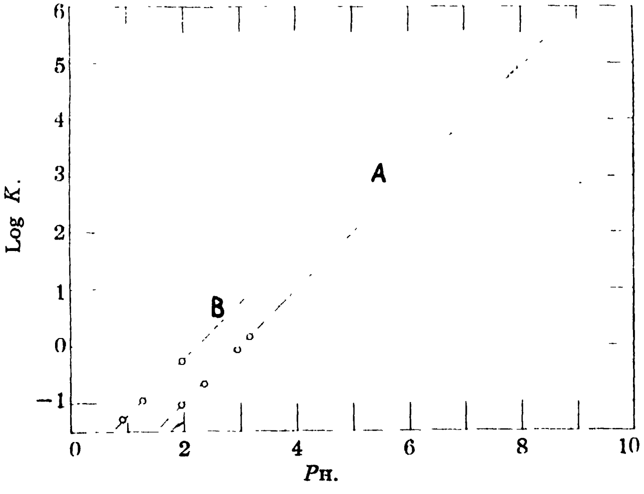

Fig. 1.—The change in rate of decomposition with P_H at 25°. Curve A, formocholine chloride; Curve B, hydroxymethyltriethylammonium chloride.

$$-d(C)/dt = k(C) \qquad (7)$$

at constant hydrogen-ion concentration. The slope of the line has a value

−0.908 and $K = 0.209$ (min.$^{-1}$). Table II summarizes similar data at different P_H values, for both formocholine chloride and triethylhydroxymethylammonium chloride.

TABLE II

THE DECOMPOSITION IN DIFFERENT BUFFERS

Formocholine chloride P_H	K (min.$^{-1}$)	Log K	Triethylhydroxymethylammonium chloride P_H	K (min.$^{-1}$)	Log K
2.972	0.0934	−1.03	1.925	0.0514	−1.289
3.364	.209	−0.68	2.274	.1255	−0.902
3.948	.855	− .068	2.972	.533	− .273
4.158	1.420	.152			

The data in Table II are plotted in Fig. 1. The slope of the drawn lines is unity, indicating that the specific reaction rate constant is inversely proportional to the hydrogen-ion concentration:

$$\log K = a + P_H \tag{8}$$

The constant a has a value characteristic of each compound; for formocholine chloride it is −4.017, for triethylhydroxymethyl ammonium chloride it is −3.213. At 25° and at a given P_H the specific reaction rate of the latter is 5.75 times that of formocholine chloride. The salt effect on the reaction rate is small. A three-fold dilution of the buffer salt caused a decrease of only 2.2% in the specific reaction rate. The P_H value of the buffered solution was considered unchanged by the dilution.

Discussion of Results.—The relative stability, compared to formocholine chloride, of its O-ethyl and O-acetyl derivatives strongly indicates that the presence of the hydroxyl hydrogen is essential to the rapidity of the decomposition. The inverse proportionality of the rate to hydrogen-ion concentration could be interpreted as a direct proportionality to hydroxide-ion concentration, but the fact that the reaction proceeds so rapidly in acid solution makes it improbable that a second order reaction involving hydroxyl ion could be concerned.

This conclusion could best be tested by determining the rate in more alkaline media. If step B in Equation (1) is the rate determining step, then the rate law should be

$$-\frac{d(C)}{dt} = \frac{k_r \cdot K_a \cdot (C)}{K_a + (H^+)} \tag{9}$$

where K_a is the equilibrium constant of step A (Equation (1)), or the acid dissociation constant of formocholine, k_r the specific reaction rate constant of step B and C the sum of the concentrations of the dissociated and undissociated reactant. If K_a is small compared to (H^+), Equation (8) takes the form of Equation (6), at constant (H^+). When K_a equals (H^+), then the observed rate constant k is equal to $^1/_2k_r$. At higher alkalinity, k approaches k_r and the slope of the curve in Fig. 1 becomes zero. The dotted line in Fig. 1 is calculated from the relation $k = k_r \cdot K_a/(K_a +$

(H^+)) assuming a value of 1×10^{-10} for K_a. The rapidity of the reaction in neutral or alkaline solution prevents a direct determination of the form of the curve in this region. The constant a (Equation (7)) is equal to log $K_a \cdot k_r$. K_a is probably of the order of 1×10^{-10}, for formocholine, in which case k_r is of the order 1×10^6 (min.$^{-1}$) at 25°.[10]

The effect of the alkyl groups is interesting and will be further studied. The same difference between methyl and ethyl groups was found by Stewart and Bradley[11] for the reaction $R_2N^+H—CH_2—SO_3^- \longrightarrow R_2N^+{=}CH_2 + HSO_3^-$. The ratio of the rates of the diethyl and dimethyl derivation was 2.6 at 30°, with very nearly the same heats of activation, as compared to a ratio of 5.75 in the formocholines. This suggests possible similarities in these apparently different types of reaction and points to the importance of the intensity and distribution of the charge on the nitrogen as one governing factor in the rate of reaction.

Summary

Trimethylhydroxymethylammonium chloride (formocholine) and triethylhydroxymethylammonium chloride have been prepared. The rates of decomposition in dilute acid have been measured and the rate law found to conform to the equation

$$R_3N^+—CH_2OH \overset{\text{Fast}}{\rightleftharpoons} R_3N^+—CH_2O^- + H^+ \xrightarrow{\text{Slow}} R_3NH^+ + CH_2O$$

The reaction is first order at constant P_H and the rate is inversely proportional to the hydrogen-ion concentration in dilute acid. The bearing of these facts on quaternary ion decomposition is discussed. The specific reaction rates are given by the equation $\log K = a + P_H$, where a has the values -4.017 and -3.213 for the trimethyl and triethyl derivatives, respectively, at 25° and when K is given in min.$^{-1}$.

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[10] A plot of $1/k$ against (H^+) should give $1/k_r$ at the intercept where (H^+) is zero. The accuracy of the data is not sufficient to make this extrapolation reliable, since $1/k_r$ is such a small number. Such a plot gives an intercept at the origin

[11] Stewart and Bradley, THIS JOURNAL, 54, 4183 (1932)

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermodynamic Properties of 2-Methylpentanol-2

BY FRANK HOVORKA, H. P. LANKELMA AND C. K. NAUJOKS

I. Introduction.—This is the first part of an investigation dealing with the effect of various types of branching of a saturated hydrocarbon chain upon the physical properties of its monohydroxyl derivatives. The hexanols were selected because the preparation of any of them in a high degree of purity and in sufficient quantity for study is reasonably convenient and because they consist of seventeen structural isomers, a number sufficiently large to offer promise in searching for general relations between physical properties and chemical constitution.

II. Preparation of 2-Methylpentanol-2.—Normal propyl bromide was slowly added to a mixture of dry ether and magnesium turnings. From the resulting Grignard reagent the crude 2-methylpentanol-2 was obtained by the method of Deschamps.[1] This product was then fractionated and the fraction boiling between 119 and 124° was collected. This fraction was further purified by fractional distillation from aluminum amalgam as the drying agent. The column used was a bead-filled Pyrex tube, 2 cm. by 108 cm., equipped with a liquid divided still head. The temperature around the column was kept at 110° by means of an asbestos covered nichrome heating coil. Distillation of 300 cc. of crude 2-methylpentanol-2 yielded about 200 cc. of alcohol with a boiling range of one degree, 120.5–121.5°; and two fractionations of this product yielded about 125 cc. of alcohol boiling over a range of 0.03°. This latter fraction was used in the determination of the physical constants.

III. Apparatus and Procedure. Temperature Control.—In all the measurements with the exception of index of refraction, Dewar flasks were used as containers for the thermostatic baths. The temperature around 25° was controlled within 0.005°. At higher temperatures the control was not as low, but even at the highest temperature, 123°, the variation did not exceed 0.05°.

Vapor Pressure and Boiling Point.—The vapor pressure was determined by using Smith and Menzies'[2] "Static isoteniscope." The boiling point of the alcohol was obtained from the vapor pressure–temperature curve.

Surface Tension.—The capillary rise method was used and the apparatus employed was similar to that described by Richards and Coombs.[3] A cathetometer accurate to 0.001 cm. was used to measure the rise.

Viscosity.—A method described by Bingham[4] was followed. How-

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(1) Deschamps, THIS JOURNAL, **42**, 2670 (1920).

(2) Smith and Menzies, *ibid.*, **32**, 1412 (1910).

(3) Richards and Coombs, *ibid.*, **37**, 1654 (1915).

(4) Bingham, *J. Ind. Eng. Chem.*, **6**, 233 (1914); Bingham and Jackson, *Bur. Standards Sci. Paper* No. 298.

ever, some changes were made to keep the driving pressure constant, so that checks within 0.01% were obtained.

The other physical properties were determined by the usual methods.

IV. Discussion of Results.—The vapor pressure and temperature were found to be related by the Rankine formula, $\log P = -(4607.5/T) - 14.6555 \log T + 52.61145$, where P is pressure in mm. of mercury and T the absolute temperature. The average deviation of the calculated vapor pressure from the observed is about 0.6% over most of the range.

The boiling point of the alcohol was found by interpolation to be 121.09 ± 0.03° at a pressure of 760 mm. This value is within the range of other reported values.

The heat of vaporization obtained from the slope of a curve by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature was about 9700 cal. at the boiling point. Calculation from the Clausius–Clapeyron equation yields a value of 9540 near the boiling point. The freezing point found was −103 ± 1.5°.

TABLE I

SURFACE TENSION, DENSITY, INDEX OF REFRACTION, VISCOSITY, VAPOR PRESSURE, SUGDEN'S PARACHOR AND EÖTVÖS CONSTANT OF 2-METHYLPENTANOL-2

Temp., °C.	Surface tension	Absolute density	Index of refraction	Absolute viscosity	Vapor pressure in mm.	Parachor observed	Eötvös constant
5.0	24.61	0.82602	1.4183			270.21	1.83
15.0	23.77	.81712	1.4138		3.1	275.80	1.74
25.0	22.90	.80970	1.4089	0.02194	8.6	276.05	1.86
35.0	22.05	.80112	1.4039	.01631	16 5	275.50	1.37
45.0	21.16	.79235	1.3993	.01245	28.2	277.97	1.76
55.0	20.46	.78304	1.3939	.00994	49.4	277.85	2.20
65.0	19.62	.77374	1.3890	.00784	83.2	277.85	2.25
75.0	18.62	.76434	1.3835	.00644	131.9	277.84	2.28
85.0	17.60	.75413	1.3781	.00537	204.2		
95.0				.00456	305.7		
105.0				.00394	446.5		
115.0				.00345	622.9		
123.0					809.6		

The rate of change of five of the physical properties (Table I) was found when plotted to deviate somewhat in the temperature range 40 to 60°. This is well shown also in the table where the calculated value of parachor decreases from 15 to 45° and then again increases. The value of Eötvös constant decreases from 1.83 to 1.37 and then increases to 2.20 above 65°. This would indicate a fairly normal liquid above 60° and association below this temperature. Judging from the other properties there is no reason to believe that there is a slow transformation from one to another form of the alcohol. But should it be a fact it is hoped to discover it when the specific heat of the alcohol is measured.

The physical constants of the other hexanol are being measured at present and their values will be reported in later communications.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Temperature-Composition Relations of the Binary System Magnesium Nitrate–Water

BY WARREN W. EWING, JOHN D. BRANDNER, C. BYRON SLICHTER AND WILLIAM K. GRIESINGER

Mention is made of several hydrates of magnesium nitrate in the literature:[1] namely, the ennea, hexa, tri, di and monohydrates and the anhydride. The purpose of this investigation was to establish definitely which of these forms actually occur in order that they might be prepared for calorimetric and vapor pressure measurements which are being made in this Laboratory. The existence of the ennea, the hexa, and the dihydrate and the anhydride has been confirmed and the conditions under which they exist are indicated by the accompanying data.

Experimental Method.—The freezing point method was used. An approximate preliminary freezing point was first determined outside the apparatus. The accurate freezing point was then determined in the apparatus, with only a fraction of a degree of supercooling. This was repeated until the accurate temperature was definitely established. The apparatus used has been described in a previous article.[2]

The following modifications were used. For temperatures below 0° a platinum resistance thermometer was used. The resistance was measured by means of a Mueller type temperature bridge made by Eppley Laboratory, Inc. The bath surrounding the freezing point tube consisted of alcohol cooled by means of solid carbon dioxide. For the higher temperatures the bath surrounding the freezing point tube consisted of oil. It contained a resistance coil extending from the top to the bottom of the oil. The oil was stirred by a stream of air bubbling through it.

C. P. magnesium nitrate was thrice recrystallized as hexahydrate from water. These crystals were dried over 60% sulfuric acid. The dihydrate was prepared by drying the hexahydrate over phosphorus pentoxide. It was possible to remove still more water by drying over phosphorus pentoxide at 110°.

The composition of the samples was determined by igniting to the oxide and weighing.

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[1] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, Vol. IV, pp. 379–381, 1923.

[2] Ewing, Krey, Law and Lang, THIS JOURNAL, 49, 1958 (1927).

Results

The data obtained are tabulated in Table I and are plotted in Fig. 1. The composition of the hexahydrate and the dihydrate follows from the diagram. The composition of the enneahydrate was determined experimentally by analysis. While this investigation was being carried out, Sieverts and Petzold[3] published results on the same system. Their data are also plotted in Fig. 1. The general shapes of the curves are similar. The discordances in results are indicated by the following comparisons, in which the first data are by the present authors and the second by Sieverts and Petzold.

TABLE I

TEMPERATURE–COMPOSITION RELATIONS

$Mg(NO_3)_2$, %[a]	Temp., °C.	Solid[b] phase	$Mg(NO_3)_2$, %	Temp., °C.	Solid phase
0.50	− 0.232	Ice	52.4	77.6	VI
1.96	− 0.476	Ice	54.0	84.3	VI
2.87	− 1.29	Ice	55.8	87.8	VI
6.58	− 2.49	Ice	57.8	89.9	VI[c]
12.09	− 5.07	Ice	61.2	87.6	VI
15.04	− 6.84	Ice	64.2	81.2	VI
18.8	−10.09	Ice	64.7	74.8	VI
22.2	−13.82	Ice	66.4	64.5	VI
25.5	−17.88	Ice	66.8	62.3	VI
27.5	−20.17	Ice	67.2	56.9	VI
29.3	−22.58	Ice	69.0	40.4	VI[d]
31.06	−25.66	Ice		52.7	VI–II
32.37	−31.87	Ice IX	68.7	52.9	II
32.8	−30.5	IX	68.4	61.1	II
33.6	−25.0	IX	69.3	65.9	II
36.6	−15.3	IX	69.4	68.6	II
37.1	−14.7	IX–VI	70.0	71.8	II
36.7	−23.7	VI[d]	71.4	82.3	II
38.4	− 4.8	VI	71.4	85.4	II
39.6	+ 2.7	VI	73.0	96.5	II
40.4	10.2	VI	74.9	114.4	II
42.5	25.0	VI	76.1	119.7	II
43.2	32.4	VI	77.5	125.8	II
45.0	43.1	VI	79.8	130.0	II
46.7	49.3	VI	81.1	130.9	II[c]
47.8	56.2	VI	82.4	130.0	II[d]
48.4	60.0	VI	81.9	130.5	II–0
49.2	63.3	VI	82.1	137.7	0
50.2	66.8	VI	82.4	144.6	0
51.5	74.1	VI			

[a] % = g. $Mg(NO_3)_2$ per 100 g. of solution. [b] IX = enneahydrate, VI = hexahydrate, II = dihydrate, 0 = anhydride. [c] = freezing point of hydrate. [d] = metastable solid phase.

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(3) Sieverts and Petzold, *Z. anorg. allgem. Chem.*, **205**, 113 (1932).

Composition	Freezing points, °C.	
Cryohydric point	−31.9	−31.5
Ennea-hexa transition	−14.7	−17.1
Hexahydrate	89.9	89.2
Hexa-di eutectic	52.7	55.6
Dihydrate	130.9	129.3
Di-anhydride eutectic	130.5	127.7

In addition to the above forms they report a metastable tetrahydrate freezing just below the hexa-di eutectic and forming hexa-tetra and tetra-di transition points. We did not find such a phase either by freezing point or vapor pressure methods.

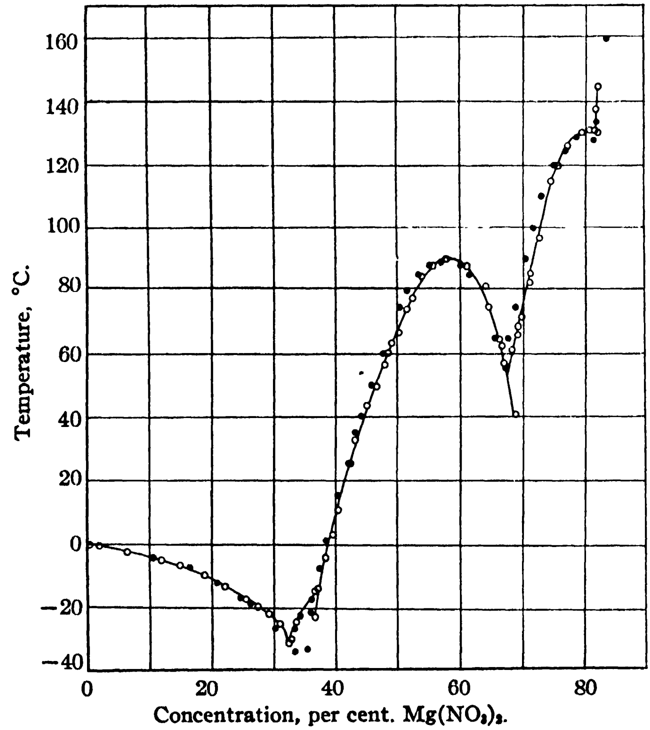

Fig. 1.—Freezing point–composition diagram of the system magnesium nitrate–water; ○, Ewing, Brandner, Slichter, and Griesinger; ●, Sieverts and Petzold.

Summary

The temperature–composition diagram of magnesium nitrate–water has been investigated.

The existence of the ennea, the hexa and the dihydrates, and of the anhydride of magnesium nitrate has been confirmed.

BETHLEHEM, PENNSYLVANIA

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Solubility Relations of the Ternary System Magnesium Nitrate-Nitric Acid-Water at 25°

BY WARREN W. EWING AND ERNST KLINGER

This further investigation[1] was undertaken to confirm the existence of certain hydrates of magnesium nitrate; and to determine methods of preparation of these salts for calorimetric and vapor pressure measurements, which are being made in this Laboratory. Malquori[2] investigated this system at 20°, but gives only fragmentary data up to 59.38% nitric acid.

Experimental

The procedure was to make saturated solutions, and to analyze both the solution phase and the moist crystal phase for nitric acid and for zinc nitrate.

Materials.—C. P. magnesium nitrate was prepared as previously described.[1] C. P. nitric acid was prepared by distilling from a mixture of two volumes of sulfuric acid and one volume of nitric acid. The distillate was redistilled in a still having a long fractionating column and a controlled reflux. The fraction distilling over at 82° was collected. This brown acid which distilled over was decolorized by blowing dry air through it at 70°. The acid thus purified analyzed 99-100% acid. A good grade of distilled water was used.

Preparation of Saturated Solutions.—Mixtures of the proper concentrations were made by weighing out requisite amounts of the three constituents. These were placed in two ounce tincture bottles having carefully ground glass stoppers. These bottles were then sealed with paraffin. The samples were then revolved in a water-bath at 25 ± 0.02° for six hours. The concentration did not change after the third hour. The saturated solution phase was then removed and analyzed. The moist residues were analyzed in enough cases to establish the nature of the solid phase.

The saturated solutions were withdrawn by either of two methods. For the non-viscous solutions, where the crystals settled out rapidly leaving a clear solution, the solution was pipetted off. In other cases, a filtering apparatus was used. It consisted of a wide-mouthed bottle having a two-holed rubber stopper. One hole contained a suction tube, and the other hole contained a tube having a sintered glass filter plate at the end. This tube, at 25°, was placed in the solution and suction was applied. This caused the saturated solution to be transferred to the wide-mouthed bottle.

Method of Analysis.—The magnesium nitrate content was determined by igniting duplicate samples to the oxide. The acid content was determined by diluting duplicate samples to one liter each and titrating 25-ml. portions with 0.1 *N* carbonate free potassium hydroxide. Either brom thymol blue or brom cresol green was used as the indicator. To ensure that the stoichiometric equivalent of base was used, the 25-ml. samples were diluted with water containing the indicator. The acidity of this diluting water had been adjusted to the indicator end-point and the diluted sample was then titrated to the same color. The amount of water was obtained by the difference between the weight of sample and the sum of the weights of the other two constituents.

Results

The data obtained are tabulated in Table I, and are plotted in Fig. 1. The solutions lying along portion AB of the curve are in equilibrium with

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[1] Ewing, Brandner, Slichter and Griesinger, THIS JOURNAL, **55**, 4822 (1933).

[2] Malquori, *Gazz. chim. ital.*, **58**, 209 (1928).

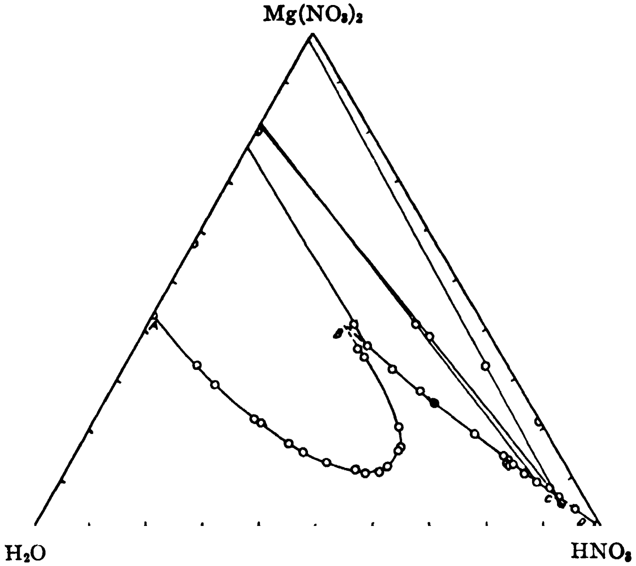

Fig. 1.—Ternary diagram of magnesium nitrate–nitric acid–water.

hexahydrate crystals, along BC with dihydrate crystals and along CD with anhydride crystals.

TABLE I

COMPOSITION OF SATURATED SOLUTIONS

%HNO_3	%$Mg(NO_3)_2$	Solid phase[c]	%HNO_3	%$Mg(NO_3)_2$	Solid phase[c]
0.0	42.5	VI	40.9	34.3	VI
12.6	33.2	VI	41.0	34.3	VI
17.9	29.0	VI[a]	41.5	34.7	VI
17.9	29.1	VI	39.6	36.0	VI
18.5	28.6	VI	41.0	36.7	II[b]
18.6	28.5	VI	47.4	32.2	II
28.1	22.0	VI	47.6	32.1	II
28.1	22.1	VI	54.8	27.6	II
29.7	21.2	VI	58.4	25.2	II
29.9	21.2	VI	68.5	19.0	II
36.7	17.1	VI	75.8	14.7	II
36.8	17.2	VI	77.0	13.0	II
37.4	16.7	VI	77.0	13.7	II
40.4	15.4	VI	77.6	12.8	II
45.4	13.2	VI	78.3	13.0	II
51.1	11.7	VI	81.2	11.0	II
53.0	11.3	VI[a]	81.9	10.6	II
55.4	11.5	VI	84.4	9.4	II[b]
55.5	11.5	VI	87.1	8.1	II[b]
56.1	12.6	VI	89.5	6.4	II
56.2	12.6	VI	89.7	6.2	II

TABLE I (*Concluded*)

%HNO₃	%Mg(NO₃)₂	Solid phase[c]
56.7	15.9	VI
56.7	16.5	VI
56.8	16.6	VI
54.6	20.2	VI[a]
91.0	4.7	0[b]
93.9	3.8	0
99.6	0.2	0[b]

[a] Dried crystals analyzed. [b] Residue analyzed. [c] VI = hexahydrate, II = dihydrate. 0 = anhydride.

The nature of the solid phase was determined by two methods. In the case of the hexahydrate, the moist residues in three instances were centrifuged, and the crystals analyzed. The values obtained were 6.16, 6.2 and 6.0 molecules of water per molecule of magnesium nitrate. The dihydrate and the anhydride were so hygroscopic that this method was not feasible. Here the "tie line" method was used. The total residue was dissolved in a weighed amount of water, and its composition determined by analysis. The "tie lines" are plotted on Fig. 1, and indicate the existence of the solid phases mentioned above.

Summary

The equilibrium diagram for the ternary system magnesium nitrate–nitric acid–water at 25° has been established.

The forms of magnesium nitrate in stable equilibrium with nitric acid at 25° are the hexahydrate, the dihydrate and the anhydride.

BETHLEHEM, PENNSYLVANIA

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Temperature-Composition Relations of the Binary System Zinc Nitrate–Water

BY WARREN W. EWING, JOHN J. MCGOVERN AND GEORGE E. MATHEWS, JR.

Mention is made of several hydrates of zinc nitrate in the literature:[1] namely, hydrates containing one, one and one-half, two, three, four, five and one-half, six and nine molecules of water. The existence of the enneahydrate and the hexahydrate have been thoroughly substantiated by previous investigators. Comprehensive solubility data are given in "International Critical Tables" for the enneahydrate and the hexahydrates. The data indicate that the next lower form is the trihydrate.

In connection with vapor pressure and calorimetric work which is being carried out in this Laboratory, it became necessary to establish definitely

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(1) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, Vol. IV, p. 651, 1923.

which hydrates of zinc nitrate exist, and to determine methods for preparing them. The freezing point method was used, and the complete solubility relations determined from the hexahydrate to the monohydrate. From the data obtained, it may be seen that the stable forms existing at room temperature are the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate.

Experimental Method

The apparatus used and the experimental technique have been described in a previous article.[2]

Materials.—A c. p. grade of zinc nitrate was recrystallized twice from water in the hexahydrate form. These crystals could be air dried on a day when the humidity was low. Desiccating the hexahydrate over concentrated sulfuric acid gave approximately the dihydrate composition. The process was very slow. Further desiccation over phosphorus pentoxide in a vacuum resulted in approximately the monohydrate composition. There was some decomposition as indicated by an insoluble residue when the salt was dissolved in water. Hence the following alternate rapid method was used to obtain the

Table I

Temperature–Composition Relations

$Zn(NO_3)_2$, %[a]	Temp., °C.	Solid phase[b]
56.1	25.1	VI
56.3	25.9	VI
56.9	27.3	VI
57.6	28.8	VI
57.7	29.1	VI
58.2	29.7	VI
58.3	30.4	VI
59.1	31.4	VI
58.9	31.4	VI
59.2	31.6	VI
59.5	32.4	VI
60.3	33.3	VI
60.3	33.4	VI
60.8	34.1	VI
61.0	34.3	VI
63.4	36.1	VI
63.7	35.9	VI
65.2	35.4	VI
66.2	34.6	VI–IV
67.4	33.1	VI[c]
67.9	40.0	IV
70.0	43.2	IV
72.5	44.7	IV
75.8	42.4	IV
76.3	41.3	IV
77.2	39.7	IV
77.3	39.1	IV
77.8	38.2	IV
77.8	37.5	IV
78.0[d]	37.2	IV–II
79.0	32.2	IV[c]
79.7	43.6	II
79.8	44.9	II
80.1	46.6	II
81.6	50.6	II
81.9	51.9	II
84.0	55.4	II
85.2	55.2	II
86.0	53.8	II
86.0	53.3	II
86.3[d]	52.1	II–I
86.6	52.8	I
86.6	54.1	I
87.6	59.2	I
88.6	65.2	I
89.0	66.9	I
89.4	68.6	I
89.8	70.3	I
90.0	70.7	I

[a] % = g. $Zn(NO_3)_2$ per 100 g. of solution. [b] VI = hexahydrate, IV = tetrahydrate, II = dihydrate, I = monohydrate. [c] Metastable solid phase. [d] Determined graphically.

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(2) Ewing, Brandner, Slichter and Griesinger, This Journal, 55, 4822 (1933).

very concentrated "melts." Hexahydrate crystals were melted and boiled until the boiling point reached 250°. There was considerable decomposition. The solution was cooled and carefully neutralized with 100% redistilled nitric acid. This neutralized sample left no insoluble residue when dissolved in water, and the solution was neutral to brom thymol blue.

Analysis.—The melts were analyzed by igniting to the oxide.

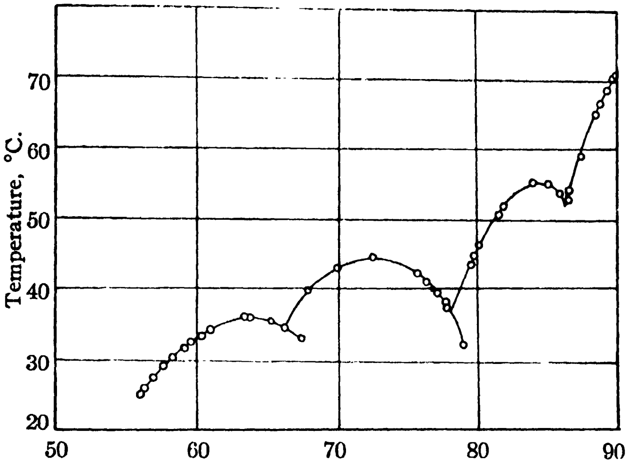

Fig. 1.—Freezing point-composition diagram of the system zinc nitrate-water.

Results

The data obtained are tabulated in Table I, and are plotted in Fig. 1. The data indicate that the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate, melting respectively at 36.1, 44.7, 55.4 and 70.7°+ are the stable forms at room temperature. No evidence was obtained of the existence of the trihydrate. It is estimated that the data are acccurate to 0.1% for the hexahydrate and the tetrahydrate regions. For the higher concentrations, the accuracy is not quite so good due to the fact that these solutions decompose slowly at their melting temperatures. All the solutions which were studied can be easily supercooled to room temperature. At the higher concentrations the solutions were quite viscous. The freezing point method is not as accurate for highly viscous liquids due to the slow formation of the crystals, and the consequent slow evolution of heat. However, the solubility method is perhaps more inaccurate due to difficulty in filtering the highly viscous system.

Summary

The solubility-temperature diagram for the system zinc nitrate-water has been extended from the hexahydrate region to the freezing point of the monohydrate.

The existence of the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate has been established.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Solubility Relations of the Ternary System Zinc Nitrate–Nitric Acid–Water at 25°

BY WARREN W. EWING, ATWOOD J. RICARDS, WILLIAM J. TAYLOR, JR., AND DAVID W. WINKLER

This further investigation[1] was undertaken to confirm the existence of certain hydrates of zinc nitrate, and to determine methods of preparation of these salts for calorimetric and vapor pressure measurements which are being made in this Laboratory. Malquori[2] investigated this system at 20°, but gives only fragmentary data for the hexahydrate and the tetrahydrate regions.

Experimental

The apparatus and the technique used have been described in a previous article.[3] The only change was to use glass wool instead of a sintered glass plate as the filter medium. This was necessitated by the viscous solutions encountered. The glass wool was packed in a bell-shaped portion extending beyond a constriction in the filtering tube. All solutions were filtered.

The methods of preparing and purifying the zinc nitrate and the nitric acid, and the methods of analysis, have been described in previous articles.[1,3] The compositions of the solid phases were established by analyzing the moist residues and plotting "tie lines."

TABLE I

COMPOSITION OF THE TERNARY SYSTEM $Zn(NO_3)_2$–HNO_3–H_2O AT 25°

Solution		Residue		
% HNO_3	% $Zn(NO_3)_2$	% HNO_3	% $Zn(NO_3)_2$	Solid phase[a]
0.0	56.1			VI
3.5	53.1			VI
9.5	49.4			VI
15.5	46.8			VI
16.6	47.6	6.1	57.8	VI
15.5	49.7	10.3	56.0	VI–IV
24.0	41.5			IV
36.7	34.6			IV
38.6	34.5	22.1	50.7	IV
39.2	35.0			IV

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(1) Ewing, McGovern and Mathews, THIS JOURNAL, 55, 4827 (1933).

(2) Malquori, *Gazz. chim. ital.*, 58, 209 (1928).

(3) Ewing and Klinger, THIS JOURNAL, 55, 4825 (1933).

TABLE I (*Concluded*)

Solution		Residue		
% HNO_3	% $Zn(NO_3)_2$	% HNO_3	% $Zn(NO_3)_2$	Solid phase[a]
38.0	37.5			IV
35.1	41.4			IV
31.6	45.9			IV
24.5	54.0	17.1	59.6	IV
18.5	60.5	11.6	64.9	IV
16.8	62.2	11.9	65.5	IV[b]
14.9	64.2	10.2	66.9	IV[b]
17.9	62.2	9.9	68.9	IV–II
12.8	65.9	11.9	67.0	II[b]
22.6	57.9	14.9	66.4	II
26.6	55.2			II
42.1	44.6			II
43.5	44.9			II
42.2	46.7			II
36.9	52.6	20.0	67.4	II
37.4	52.1	9.0	81.8	I
47.4	43.5	22.0	69.1	I
64.6	28.9			I
65.5	28.1			I
78.9	15.3			I
85.9	11.6	42.9	51.3	I
86.9	10.9			I
88.5	10.1			I
88.8	9.9			I

[a] VI = hexahydrate, IV = tetrahydrate, II = dihydrate, I = monohydrate

[b] Metastable solid phases.

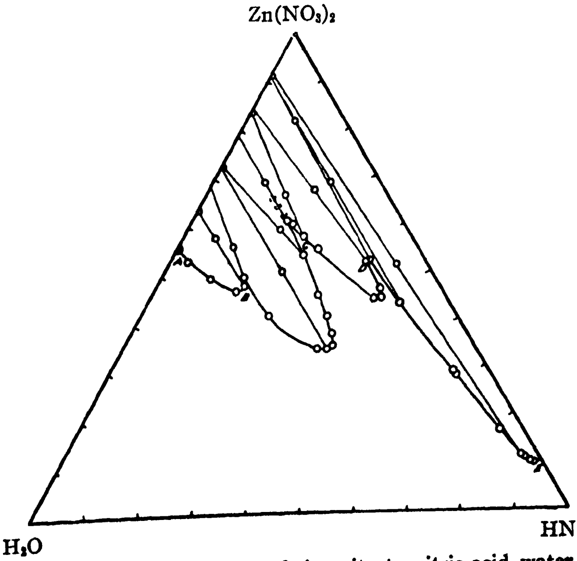

Fig. 1.—Ternary diagram of zinc nitrate–nitric acid–water.

Results

The data obtained are tabulated in Table I, and plotted in Fig. 1. The saturated solutions lying along portion AB of the curve are in equilibrium with the hexahydrate crystals; along BC, with the tetrahydrate; along CD, with the dihydrate, and along DE, with the monohydrate. These are the same hydrates that were found by the freezing point method for the binary system zinc nitrate–water.[1] No evidence was obtained of the existence of the trihydrate.

Summary

The equilibrium diagram for the ternary system zinc nitrate–nitric acid–water at 25° has been established.

The forms of zinc nitrate in stable equilibrium with nitric acid at 25° are the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate.

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[CONTRIBUTION FROM THE GAYLEY CHEMICAL LABORATORY OF LAFAYETTE COLLEGE]

The Fluidity of Dioxane–Water Mixtures[1]

BY JOHN A. GEDDES

I. Introduction

Because of the wide range of dielectric constants which can be obtained by the use of dioxane–water mixtures, these have become of considerable importance in the study of dilute electrolytic solutions.[2] The viscosity is also a contributing factor in this study, and although some measurements have already been made,[3] it is evident that corrections are necessary, the value of a 10% water–90% dioxane mixture at 20° being obviously in error. In addition, the fluidity–temperature plot of pure dioxane does not give the smooth curve which should be obtained. This is doubtless caused by incomplete purification, the melting point of the dioxane used having been reported as 11.0°, whereas a later method[4] affords a compound melting several tenths of a degree higher.

This investigation was undertaken to examine the effect of addition of water on the fluidity of dioxane, to correct existing data, and to furnish data at 25° in particular for application to the study of the conductivity of dilute solutions in these mixtures.

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(1) The author wishes to express his appreciation to Dr. Eugene C. Bingham, who afforded the facilities of his laboratory for this investigation.

(2) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933), Fuoss and Kraus, *ibid.*, **55**, 476 (1933), **55**, 1019 (1933).

(3) Herz and Lorentz, *Z. physik. Chem.*, **140**, 407 (1929).

(4) Vingee, Thesis, Brown University, 1931.

II. Apparatus and Materials

Viscosities were measured in a variable pressure viscometer[5] number 1–33, calibrated at 20° with pure distilled dust-free water, a viscosity of 1.005 c. p. being assumed at that temperature. The values of the instrument constants[6] obtained were $C = 1.70756 \times 10^{-7}$, $C' = 0.01593$, $m_l = 1.43$, and $m_r = 1.32$.[7] The hydrostatic head correction[7,8] was negligible. The value of C was the average of eight determinations on two samples of water, the extreme deviation being 0.08%. The m's were averaged from nine determinations of flow in each direction, three samples being used for this purpose.

Temperatures were kept constant within 0.02° by the use of thermometer number 36,715, calibrated at the Physikalisch-Technische Reichsanstalt and the U. S. Bureau of Standards. Stem corrections were made when necessary.

Densities were determined by the use of pycnometer 2-33, except in the case of pure dioxane, which was measured in pycnometer 1-31, calibrated by means of water, and corrected to vacuum.

Dioxane was purified by a modified form of Vingee's method.[4] The technical product was cooked with caustic soda, dried over barium oxide and then twice boiled with metallic sodium. The dioxane was then distilled, and fractionally crystallized, the first fraction being refluxed for several hours over sodium–lead alloy, and finally distilled over this before use. The melting point after removal from the viscometer was 11.6°.

III. Results

The experimental results are summarized in Tables I–III, where the temperature is in degrees centigrade, the viscosity is in centipoises, and

TABLE I

VISCOSITIES OF DIOXANE–WATER MIXTURES

% Water	20°	25°	30°	40°	60°	80°
0.000	1.3076	1.1964	1.0990	0.9416	0.7146	0.5625
(Pure dioxane)	1.3079	1.1966	1.0992	.9414	.7149	.5624
	1.3071	1.1976	1.1003	.9415	.7145	.5629
	1.3072	1.1969	1.1005	.9414	.7149	.5626
0.975	1.3055	1.1962	1.0978	.9391	.7121	.5618
	1.3060	1.1959	1.0984	.9391	.7116	.5615
2.079	1.3200	1.2067	1.1077	.9443	.7138	.5619
	1.3199	1.2067	1.1068	.9440	.7135	.5613
5.018	1.3992	1.2745	1.1627	.9839	.7338	.5706
	1.3998	1.2739	1.1629	.9835	.7341	.5707

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(5) Bingham, *Proc. A. S. T. M.*, **18**, Pt. II, 373 (1918); also U. S. Bur. of Standards, Bull. 298, 14 (1917).

(6) Bingham, "Fluidity and Plasticity," Appendix A.

(7) Bingham and Geddes, *Physics*, **4**, 203 (1933).

(8) Corrected for typographical error, this equation should read $h_l = [(t_l - t_r)/(t_l + t_r)][p/\rho + C'/Ct_lt_r]$.

TABLE I (*Concluded*)

% Water	20°	25°	30°	40°	60°	80°
10.96	1.6215	1.4578	1.3215	1.0998	0.8007	0.6079
	1.6191	1.4581	1.3212	1.0997	.7996	.6075
21.33	1.9816	1.7606	1.5743	1.2790	.8956	.6611
	1.9810	1.7609	1.5739	1.2787	.8951	.6608
44.26	2.2637	1.9760	1.7383	1.3774	.9246	.6632
	2.2632	1.9748	1.7381	1.3761	.9242	.6624
56.94	2.0599	1.7962	1.5797	1.2505	.8433	.6100
	2.0598	1.7962	1.5790	1.2506	.8430	.6099
75.91	1.5768	1.3802	1.2213	0.9756	.6713	.4949
	1.5762	1.3807	1.2211	.9755	.6707	.4949
88.55	1.2579	1.1090	0.9855	.7973	.5584	.4189
	1.2585	1.1084	.9853	.7976	.5587	.4191
100.00	1.0044	0.8928	.7983	.6547	.4681	.3566
(Pure water)	1.0048	.8924	.7984	.6550	.4682	.3570

(The viscosity of pure dioxane was also measured at 50°, these values being 0.8158, 0.8160, 0.8154 and 0.8161. The fluidity averaged from these is 122.58 rhes.)

TABLE II

SPECIFIC VOLUMES OF DIOXANE-WATER MIXTURES

% Water	20°	25°	30°	40°	60°	80°
0.000 (Pure dioxane)	0.9667	0.9722	0.9774	0.9882	1.0118	1.0363
0.975	.9679	.9733	.9788	.9895	1.0120	1.0367
2.079	.9677	.9728	.9786	.9894	1.0117	1.0359
5.018	.9666	.9718	.9769	.9875	1.0097	1.0335
10.96	.9644	.9693	.9741	.9843	1.0054	1.0285
21.33	.9616	.9662	.9708	.9799	0.9993	1.0212
44.26	.9630	.9667	.9706	.9782	.9949	1.0140
56.94	.9680	.9713	.9747	.9815	.9964	1.0136
75.91	.9809	.9831	.9858	.9912	1.0038	1.0181
88.55	.9914	.9931	.9951	.9997	1.0098	1.0227

TABLE III

FLUIDITIES OF DIOXANE-WATER MIXTURES

% Water	20°	25°	30°	40°	60°	80°
0.000	76.48	83.55	90.93	106.21	139.92	177.75
.975	76.59	83.61	91.07	106.49	140.49	178.06
2.079	75.76	82.87	90.31	105.92	140.13	178.08
5.018	71.46	78.49	86.00	101.66	136.25	175.25
10.96	61.72	68.59	75.68	90.93	124.98	164.55
21.33	50.47	56.80	63.53	78.20	111.69	151.30
44.26	44.18	50.62	57.53	72.64	108.18	150.88
56.94	48.55	55.67	63.32	79.97	118.61	163.94
75.91	63.43	72.44	81.89	102.51	149.03	202.07
88.55	79.48	90.20	101.48	125.41	179.05	238.66
100.00	99.54	112.03	125.26	152.71	213.63	280.29

the fluidity in rhes. It will be noted that the greatest deviation between right and left limb determinations is only 0.15% for the 10.96% water mixture at 20°, and as the majority of the determinations are well within this figure, it is believed that a precision higher than the customary 0.1% has been obtained. (In Table I, left and right limb determinations are given alternately.) The viscosities of water are not absolute values, but were obtained by the use of the instrument constants derived from calibration with water at 20°, a viscosity of 1.005 c. p. being assumed at that temperature.

IV. Discussion of Results

The relationship between the fluidity of dioxane and the temperature in degrees centigrade is expressed over the range of temperature covered by the equation

$$\varphi = \frac{T - 171.97 + (T^2 - 146.58T + 39,264.2)^{1/2}}{0.51894} \qquad (1)$$

Observed and calculated values are compared in Table IV.

TABLE IV

COMPARISON OF OBSERVED VALUES OF FLUIDITY OF DIOXANE WITH VALUES CALCULATED FROM EQUATION 1

Temp., °C.	20	25	30	40	50	60	80
Observed	76.48	83.55	90.93	106.21	122.58	139.92	177.75
Calculated	76.48	83.55	90.86	106.22	122.56	139.92	177.77

By rearrangement of equation 1, we may calculate the absolute temperatures required for fluidities of 50, 100 and 200 rhes. These are listed in Table V, together with the values calculated from the atomic temperature constants,[9] and the association "n."

(n = Observed absolute temperature/calculated absolute temperature)

Extrapolated values are given in parentheses.

TABLE V

ASSOCIATION OF DIOXANE BY FLUIDITY METHOD

Fluidity in rhes	Absolute temperature Observed	Calculated	Association n
50	(272.6)	179.2	(1.52)
100	309.0	199.6	1.55
200	(364.0)	230.7	(1.58)

It is observed that the association increases with the temperature. On the other hand, the fluidity-specific volume plot shows positive curvature, thus indicating a breaking down of association. Also, this value is rather high for a compound of this type, so that some doubt is cast upon the values of the atomic temperature constants—particularly that of the oxygen atom.

The fluidity is plotted against the composition by weight of the mixtures in Fig. 1. There is an inflection point in the curves at about 5% of water—an unusual type of behavior, Bingham and Rogers[10] having found

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(9) Bingham and Spooner, *J. Rheol.*, **3**, 221 (1932).

(10) Bingham and Rogers, *ibid.*, **3**, 113 (1932).

only two examples out of one hundred and thirty-one mixtures studied. Between 5 and 100% water, the curves follow the usual course of mixtures of two liquids in which a volume contraction occurs. It has been previously noted[3] that the minimum in these curves shifts toward the region of higher dioxane concentration with increasing temperature. This effect is also seen here, the minimum being at 45% water at 20°, and at 32.5% water at 80°. This, however, is to be expected in mixtures of this type, and the minimum has no meaning. The important factor is the point of greatest deviation from linearity,[11] or in other words, the point at which the slope of the experimental curve is equal to that of the straight line connecting the fluidities of the pure components. The mean value determined from the six curves is 49.9% of water, which corresponds, within the error of reading, to a mixture of the composition $C_4H_8O_2 \cdot 5H_2O$. Assuming that the dioxane and water present uncombined have not been dissociated, it is possible to calculate the amount of the hydrate formed.

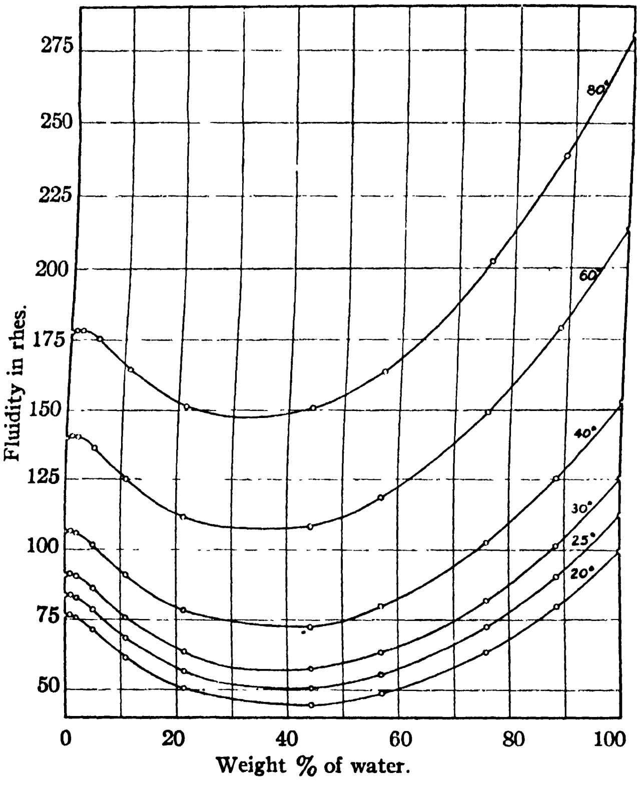

Fig. 1.—Fluidity–concentration curves of dioxane–water mixtures.

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[11] Bingham and Brown, *J. Rheol.*, 3, 95 (1932).

From the atomic temperature constants[9] it appears that this compound should have a fluidity of 100 rhes at an absolute temperature of 771.6°. By interpolation from the curves, a mixture of this composition is found to have a fluidity of 100 rhes at 326.4°. Pure dioxane and pure water attain this fluidity at 309.0 and 293.2°, respectively, so that if the mixture were wholly uncombined, the absolute temperature necessary for a fluidity of 100 rhes (using volume % of components) would be $309.0° \times 0.4918 + 293.2° \times 0.5082 = 301.0°$. Letting x represent the fraction of the volume of the mixture which is combined, we obtain $771.6°x + 301.0° (1-x) = 326.4°$, and $x = 0.054$, so that approximately 5.4% by volume of the mixture is in combination.

This value serves to indicate the order of magnitude of combination, but may be appreciably in error, because of the uncertainty of the value of the atomic temperature constants previously noted, and in a greater degree, because of the negative curvature between pure dioxane and 5% water. This indicates an increase in fluidity which is ascribed to dissociation of the highly associated water and moderately associated dioxane in this region. It will also be noted that the specific volume varies in the same manner as the fluidity; the addition of small amounts of water results in an increase in volume, whereas larger amounts result in a volume contraction.

V. Summary

1. The viscosities of dioxane, water and of nine dioxane–water mixtures have been measured over the temperature range 20–80°.

2. The variation of the fluidity of dioxane with temperature is expressed by the equation $\varphi = [T - 171.97 + (T^2 - 146.58T + 39{,}264.2)^{1/2}]/0.51894$.

3. The fluidity–concentration curves are all inflected in the neighborhood of 5% water, showing that addition of small amounts of water results in an increase in fluidity, whereas larger amounts produce the customary decrease.

4. The points of maximum deviation from linearity of the fluidity–concentration curves indicate the presence of approximately 5% of a hydrate of the formula $C_4H_8O_2 \cdot 5H_2O$.

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The Thermodynamics of Aqueous Sodium Hydroxide Solutions from Electromotive Force Measurements[1]

BY HERBERT S. HARNED AND JOHN C. HECKER

Harned and Nims[2] by measurements of the electromotive forces of the cells Ag | AgCl | NaCl (m) | Na_xHg | NaCl (0.1) | AgCl | Ag through the temperature range of 0 to 40° have computed the activity coefficient, the partial molal heat content relative to 0.1 M sodium chloride, and the relative partial molal specific heat of sodium chloride in aqueous solution. These results are the first of their kind in which cells containing sodium amalgam electrodes were employed. More recently, Harned and Ehlers by employing the cells H_2 | HCl (m) | AgCl | Ag have made a very comprehensive study of the above thermodynamic properties of hydrochloric acid in aqueous solution from 0 to 60°.[3] In order to complete a work in which we have in the first place measured the sodium amalgam electrode and in the second place the hydrogen electrode against the silver–silver chloride electrode, we have completed measurements of the cells H_2 | NaOH (m_2) | Na_xHg | NaOH (m_1) | H_2, in which the hydrogen electrode is measured against the amalgam electrode. The only earlier measurements of these cells were made by Harned, whose results were obtained at only one temperature, 25°. The present measurements are much more comprehensive and include results at 5° intervals from 0 to 35° inclusive.[4]

There is little doubt that measurements of this kind are very valuable for the determination of partial free energies and activity coefficients. Since the relative partial molal heat contents and specific heats are obtained from the first and second derivatives of the original electromotive forces great accuracy in the evaluation of these quantities is difficult to obtain. In the case of hydrochloric acid solutions, excellent agreement with the best calorimetric determinations of these quantities was attained. Amalgam cells are difficult and, consequently, it is not to be expected that so great precision is possible as with the simpler cells. We shall show, however, that good values of the heat data are obtainable.

In the case of sodium chloride solutions, Harned and Nims did not extrapolate their values of the partial molal heat content to zero concentration of salt but gave their results relative to zero at 0.1 M. An important feature of the present study is the introduction of a method of extrapolation of this quantity which we have employed not only with our results but with those of Harned and Nims.

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[1] This communication contains material from a dissertation presented by John C. Hecker, to the Graduate School in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1933.

[2] Harned and Nims, THIS JOURNAL, 54, 423 (1932).

[3] Harned and Ehlers, *ibid.*, 55, 2179 (1933).

[4] Harned, *ibid.*, 47, 677 (1925).

Materials, Experimental Technique and Electromotive Forces of the Cells: $H_2 \mid NaOH\ (m) \mid Na_xHg \mid NaOH\ (0.05) \mid H_2$.—The highest grade of sodium hydroxide purified by alcohol was used. A saturated solution was prepared and the sodium carbonate which is insoluble in this solution settled to the bottom of the flask. The clear solution was drawn off into freshly distilled carbon dioxide-free water which formed a stock solution of approximately 4 *M*. This solution was boiled under reduced pressure and kept in an atmosphere of carbon dioxide-free air. From this solution 15 liters of 0.05 *M* solution was prepared and kept under nitrogen. A glass tube led directly from the vessel containing this solution to the cells which were fixed in the thermostat. The solutions at the different concentrations in the other half of the cell were made by diluting the stock solution, were boiled under reduced pressure and kept in an atmosphere of nitrogen until introduced into the cell.

Titration with weight burets against gravimetrically analyzed hydrochloric acid solutions was employed for purposes of standardization. The concentrations were known to ±0.05%.

A type of cell similar to that employed by Harned[4] which contained flowing sodium amalgam electrodes was used. A vacuum technique was employed. One modification of the cell design should be mentioned. An additional stopcock was placed between the hydrogen and amalgam electrode compartments in each half cell. This made it possible to use the same hydrogen electrode half cells at each of the eight temperatures at which measurements were made. The cells were filled with the oxygen free solutions at 0° with the stopcock open, hydrogen electrodes were introduced and four hours allowed for them to attain equilibrium. The amalgam was allowed to flow and a measurement taken. At the end of the measurement after all the amalgam had flowed from the dropper, the stopcocks between the hydrogen and amalgam electrodes were closed. The amalgam droppers were removed and replaced by rubber stoppers. The amalgam half cells were then drained, evacuated and refilled with solution, and the amalgam introduced into the dropper. In the meantime, the thermostat temperature was raised 5°. Two hours were allowed for the cell to reach equilibrium before the 5° measurement of electromotive force was made. The same procedure was repeated for each succeeding measurement until a temperature of 35° was reached.

The hydrogen electrodes were of the usual platinized platinum foil type. The sodium amalgam was prepared as described by Harned and was approximately 0.01% by weight of sodium. The temperature control was ±0.02°.

The original electromotive forces made at fourteen concentrations and eight temperatures were of necessity at odd concentrations and were first smoothed to round concentrations. In the first place, a small correction was made to remedy the fact that the reference solution was not quite 0.05 *M*. The smoothing to round concentrations was then carried out in the following manner. The electromotive forces of the cells are given by

$$E - \frac{2RT}{NF}\ln\frac{m}{0.05} = \frac{2RT}{NF}\ln\frac{\gamma}{\gamma_{0.05}} + \frac{RT}{NF}\ln\frac{p_{0.05}}{p_m} \qquad (1)$$

where γ is the activity coefficient of sodium hydroxide in a solution of concentration *m*, and $\gamma_{0.05}$ is its activity coefficient in the 0.05 *M* reference solution. The second term on the right represents the contribution to the electromotive force produced by the transfer of water which takes place in the cell according to the equation NaOH (*m*) + H_2O (0.05) = NaOH (0.05) + H_2O (*m*). p_m and $p_{0.05}$ are the vapor pressures of water over the solutions of concentrations *m* and 0.05, respectively. A sensitive large graph was made by plotting the left side of equation (1) against $m^{1/2}$ at each temperature. From the values of this function at round concentrations, smoothed values of *E* were obtained at each temperature. At constant composition, *E* may be expressed as a function of the temperature by the equation

$$E = E_0 + at + bt^2 \qquad (2)$$

where E_0 is the electromotive force at 0°, *a* and *b* are constants and *t* is centigrade temperature. The constants were determined by the method of least squares. Table I contains the values of the electromotive forces computed by equation (2) as well as the values of the constants of this equation. Comparison with measured values is shown by parenthesized

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: H_2 | NaOH (*m*) | Na_xHg | NaOH (0.05) | H_2, CALCULATED BY EQUATION (2), AND DEVIATIONS, $E_{\text{calcd.}} - E_{\text{obs.}}$

m	*t*...0°	5°	10°	15°
0.25	0.06929	0.07070(12)	0.07207(4)	0.07341(−3)
.5	.10018	.10027(15)	.10431(3)	.10628(−8)
1	.13156	.13444(4)	.13725(−4)	.13997(0)
1.5	.15113	.15445(4)	.15767(−2)	.16082(−2)
2	.16600	.16963(3)	.17317(−2)	.17662(−2)
2.5	.17853	.18261(−17)	.18652(−9)	.19030(2)
3	.19033	.19471(−19)	.19893(−8)	.20296(−1)
3.5	.20176	.20618(−9)	.21046(−16)	.21459(−1)
4	.21261	.21711(−4)	.22148(−9)	.22572(0)

m	*t*...20°	25°	30°	35°
0.25	0.07471(3)	0.07596(−5)	0.07719(−9)	0.07839(9)
.5	.10826(0)	.11017(−1)	.11203(−6)	.11385(6)
1	.14261(−2)	.14519(1)	.14767(3)	.15007(−3)
1.5	.16386(−3)	.16682(1)	.16969(7)	.17247(−4)
2	.17997(−1)	.18322(0)	.18637(6)	.18944(−4)
2.5	.19392(5)	.19740(8)	.20072(3)	.20391(−8)
3	.20683(8)	.21050(6)	.21402(9)	.21734(−11)
3.5	.21859(17)	.22245(−1)	.22617(5)	.22973(−7)
4	.22981(0)	.23375(7)	.23758(6)	.24126(−7)

TABLE I (*Concluded*)

Constants of equation (2)

m	0.25	0.5	1	1.5
$a \times 10^6$	285	422	585	672
$-b \times 10^6$	0.73	0.90	1.59	1.79
$-b' \times 10^6$	.6	1.0	1.55	1.90

m	2	2.5	3	3.5	4
$a \times 10^6$	736	829	895	898	915
$-b \times 10^6$	1.91	2.97	2.52	2.82	2.76
$-b' \times 10^6$	2.15	2.45	2.62	2.78	2.94

figures, which give the deviations in hundredths of millivolts. The values of b were plotted against the temperature and the smoothed values b', to be used later on to compute the relative partial molal heat capacity, are also given in the table.

Activity Coefficients.—In order to compute γ, or $(\gamma_{\mathrm{Na}}\gamma_{\mathrm{OH}})^{1/2}$, it is first necessary to compute the vapor pressures of the solutions. By rearranging equation (1) and substituting k for 2.3026 RT/F, we obtain

$$\log \frac{\gamma}{\gamma_{0.05}} = \frac{E}{2k} - \log \frac{m}{0.05} - \frac{1}{2} \log \frac{p_{0.05}}{p_m} \tag{3}$$

The vapor pressure of the solvent is related to the activity coefficient of the solute by the equation

$$-\partial \ln p = \frac{\nu}{55.51} \int \partial m + \frac{\nu}{55.51} \int m \, \partial \ln \gamma \tag{4}$$

Upon substituting the limits corresponding to m and 0.05, integrating and rearranging this equation, we obtain

$$\frac{1}{2} \log \frac{p_{0.05}}{p_m} = \frac{1}{55.51} m \log \frac{\gamma}{\gamma_{0.05}} + \frac{(m - 0.05)}{55.51 \times 2.303} \tag{5}$$

The desired term on the left was evaluated by arithmetical approximation. As a first approximation the last term on the right was employed to compute this quantity. This approximate value along with E and m were substituted on the right of equation (3) and the first approximation to the logarithm of the activity coefficient ratios was obtained. With these values the first term on the right of equation (5) was evaluated graphically. This plus the last term of equation (5) served to give a closer approximation to one-half the logarithm of the vapor pressure ratio which latter when substituted in equation (3) gave a closer estimate of the logarithm of the activity coefficient ratios. This process was repeated until the values of equation (5) remained constant. Table II contains the results of this calculation at the designated molalities and at 0 and 35°. It is important to note that the temperature coefficient of the quantity in question is small and varies only in the fourth decimal place. One in this decimal place corresponds to only a difference of 0.01 mv. Consequently, the correction may be regarded as constant or independent of the temperature since this assumption is within the experimental error. As a consequence the effect of the vapor pressure ratios upon the temperature coefficient of E is negligible, a fact which is of considerable value when we come to the computations of the heat data.

TABLE II

THE VAPOR PRESSURE TERM

m	0.25	0.5	1	1.5	2	2.5	3	3.5	4
$^1/_2 \log p_{0.05}/p_m$:									
0°	0.0015	0.0033	0.0071	0.0110	0.0152	0.0197	0.0248	0.0313	0.0369
35°	.0015	.0033	.0072	.0111	.0152	.0199	.0251	.0311	.0367

The final values of log $\gamma_{0.05}$ are given in Table III. In order to obtain $\gamma_{0.05}$ from these data, we employed the equation of Hückel or equation (11) in the communication of Harned and Ehlers.[3] The values used for the constant of the Debye and Hückel theory were those computed by Harned and Ehlers and given in the second column of their Table VII. The A and B constants of this equation were evaluated and are given in Table III.

TABLE III

ACTIVITY COEFFICIENT DATA AND CONSTANTS OF HÜCKEL'S EQUATION

log $(\gamma/\gamma_{0.05})$

m	0°	5°	10°	15°	20°	25°	30°	35°
0.05	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.25	− .0611	− .0598	− .0590	− .0584	− .0592	− .0584	− .0572	− .0593
.5	− .0789	− .0765	− .0748	− .0737	− .0726	− .0721	− .0719	− .0702
1	− .0941	− .0898	− .0864	− .0838	− .0821	− .0809	− .0803	− .0807
1.5	− .0935	− .0886	− .0846	− .0813	− .0793	− .0780	− .0772	− .0774
2	− .0855	− .0802	− .0758	− .0723	− .0700	− .0685	− .0677	− .0678
2.5	− .0713	− .0640	− .0584	− .0541	− .0514	− .0501	− .0498	− .0509
3	− .0467	− .0386	− .0322	− .0276	− .0247	− .0236	− .0235	− .0245
3.5	− .0146	− .0103	+ .0024	+ .0013	+ .0034	+ .0044	+ .0047	+ .0032
4	+ .0219	+ .0275	+ .0315	+ .0343	+ .0358	+ .0360	+ .0355	+ .0337

Constants of Hückel's equation

	0°	5°	10°	15°	20°	25°	30°	35°
A	0.688	0.721	0.738	0.752	0.718	0.754	0.825	0.814
a(Å.)	3.00	3.14	3.20	3.25	3.10	3.24	3.54	3.45
B	0.0410	0.0410	0.0422	0.0432	0.0472	0.0460	0.0420	0.0434
$-\log \gamma_{0.05}$	.0861	.0859	.0861	.0863	.0868	.0875	.0871	0.0881
$\gamma_{0.05}$	.820	.821	.820	.820	.819	.818	.818	.816

Normal concentrations, c

m	0°	5°	10°	15°	20°	25°	30°	35°
0.05	0.05002	0.05002	0.05000	0.04997	0.04992	0.04986	0.04978	0.04971
.25	.2506	.2505	.2503	.2501	.2497	.2494	.2491	.2488
.50	.5023	.5020	.5015	.5010	.5003	.4998	.4988	.4980
1.0	1.0058	1.005	1.004	1.003	1.002	.9990	.9981	.9957
1.5	1.510	1.508	1.506	1.504	1.501	1.499	1.489	1.483
2.0	2.013	2.010	2.007	2.005	2.001	1.997	1.994	1.989
2.5	2.514	2.510	2.506	2.505	2.500	2.496	2.490	2.484
3.0	3.015	3.009	3.003	2.998	2.994	2.985	2.976	2.972
3.5	3.508	3.504	3.498	3.492	3.485	3.477	3.469	3.463
4.0	4.000	3.993	3.985	3.976	3.969	3.962	3.950	3.941

The values of the apparent ionic diameter, "*a*," computed from A by means of equation (12) and the values of K' in Table VII of Harned and Ehlers' paper are also given. By employing these constants, $-\log \gamma_{0.05}$ was obtained, from which the values of $\gamma_{0.05}$ given in Table III were evaluated. The concentrations *c*, in moles per liter of solution, which are necessary for these calculations are recorded in the lower part of this table.

It is important to note that the Hückel equation may be used to compute the experimental values of γ from 0.05 to 1 *M* and is not valid in the more concentrated solutions. This is similar to the behavior of hydrochloric acid in aqueous solution as found by Harned and Ehlers. We have not resorted to the additional refinements imposed by Harned and Ehlers since owing to the greater difficulties inherent in our measurements, the accuracy although good is not equal to that obtainable with the simpler cell employed by them. However, the use of the Hückel equation may be expected to yield a good extrapolation for γ and a value of $\gamma_{0.05}$ which is probably correct to within ±0.002. Incidentally, the present results at 25° agree well up to 1.5 *M* with those of Harned.[4] The values of the mean distance of approach "*a*" are reasonable. The fact that they show a tendency to increase with the temperature should not be taken seriously, since in the cases where "*a*" appears to increase, B tends to decrease. Therefore, we conclude from these results that as a first approximation "*a*" is not a function of the temperature and has a value of approximately 3.3 Å.

The Relative Partial Molal Heat Content of Sodium Hydroxide.—By the Gibbs-Helmholtz equation

$$\overline{H}_m - \overline{H}_{0.05} = NEF - NFT\,(\mathrm{d}E/\mathrm{d}T) \qquad (6)$$

the partial molal heat content relative to the 0.05 *M* solution may be computed from the electromotive forces. We desire the partial molal heat content of the hydroxide and not that of both hydroxide and water which as previously pointed out would be derived from the processes taking place within the cell. Fortunately, since the vapor pressure term in equation (3) can be taken to be independent of the temperature without interfering with the accuracy, it is only necessary to apply the vapor pressure correction to the electromotive forces and not to their temperature coefficients. Therefore, we may express the electromotive forces, *E'*, resulting from the transfer of sodium hydroxide only by

$$E' = E_0' + at + bt^2 \qquad (7)$$

whence it is obvious that the original *a* and *b* values can be employed for computing the temperature coefficients without further change.

Since we desire $\overline{L}_2$ or $\overline{H}_m - \overline{H}_0$, it is necessary for us to devise methods for the evaluation of $\overline{H}_{0.05} - \overline{H}_0$. If, as shown by Harned and Ehlers, the Debye and Hückel equations with supplementary constants permit an accurate calculation of the activity coefficients, this can be done by substitution of log γ in the Gibbs-Helmholtz equation and subsequent differentiation. In the following treatment of this subject, we have developed this method in a general manner and in a way which renders the computations relatively easy. From the equations thus derived an empirical extrapolation formula has been obtained which has proved useful in the present instance and also permits the extrapolation of the results obtained by Harned and Nims with sodium chloride solutions.

$\bar{L}_2$ may be computed from the well known equation

$$\bar{L}_2 = -\nu RT^2 \frac{\partial \ln f}{\partial T} \tag{8}$$

by substitution of the value of ln *f*, the logarithm of the "rational" activity coefficient, or the activity divided by the mole fraction, as expressed by an equation which is the equivalent of Hückel's equation. Thus

$$\bar{L}_2 = \nu RT^2 \frac{\partial}{\partial T} \left\{ \frac{z_1 z_2 e^2}{2kDT} \frac{\kappa}{1 + \kappa a} - bc \right\} \tag{9}$$

Taking *D*, *c*, *a*, *T* and *b* as variables, this differentiation gives

$$\bar{L}_2 = \nu z_1 z_2 L \frac{\sqrt{\Gamma}}{1 + \mathrm{A}\sqrt{\Gamma}} - \nu z_1 z_2 w \frac{\Gamma}{(1 + \mathrm{A}\sqrt{\Gamma})^2} \left[\frac{\mathrm{d}a}{\mathrm{d}T} + \frac{a}{z} \frac{\mathrm{d}\, ln\, \Gamma}{\mathrm{d}T} - y \right] - \nu RT^2 \left(b \frac{\mathrm{d}c}{\mathrm{d}t} + c \frac{\mathrm{d}b}{\mathrm{d}T} \right) \tag{10}$$

At constant temperature, *L*, *w*, and *y* are constants. The first term is the limiting slope resulting from the Debye–Hückel theory and is expressed by

$$L = -\frac{3}{4} \frac{Re^2\, 3.557 \times 10^9}{kD\,(DT)^{1/2}} \left(1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T} + \frac{T}{3V}\frac{\mathrm{d}V}{\mathrm{d}T} \right) \tag{11}$$

$$w = \frac{2.0635 \times 10^{16}}{D^2};\ y = \frac{1}{2T}\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T} \right]$$

By using the values of d*D*/d*T* computed from the equation according to Wyman[5] and the values of d "*d*"/d*T* obtained from the densities of water,[6] the values of *L*, *w* and *y* given in Table IV were evaluated. It is obvious that −d log *v*/d log *T* = d log "*d*"/d log *T*. "*a*" in centimeters may be

TABLE IV

VALUES OF QUANTITIES IN EQUATIONS (10) AND (16)

t, °C.	*L*	*Q*	$-y \times 10^4$	$x \times 10^8$	$w \times 10^{-12}$
0	153	3.40	8.360	4.358	2.665
5	169	3.67	9.238	4.349	2.787
10	190	3.96	10.092	4.338	2.916
15	210	4.22	10.909	4.327	3.053
20	231	4.48	11.692	4.315	3.195
25	254	4.72	12.452	4.302	3.345
30	278	4.96	13.177	4.288	3.503
35	303	5.19	13.869	4.274	3.668
40	329	5.44	14.539	4.258	3.844
45	357	5.67	15.326	4.243	4.026
50	385	5.89	15.776	4.226	4.218
55	414	6.08	16.318	4.209	4.418
60	446	6.30	16.863	4.192	4.633

Values of constants: $e = 4.774 \times 10^{-10}$; $N = 6.061 \times 10^{23}$; $k = 1.372 \times 10^{-16}$; $R = 1.9885$; 1 cal. = 4.185 joules; $F = 96{,}500$.

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(5) Wyman, *Phys. Rev.*, **35**, 623 (1930); Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III.

calculated from the parameter, A, of Hückel's equation by $a = Ax$, and b is related to the parameter B in Hückel's equation by $bc = 2.3026\ B\Gamma$. Values of x are also given in Table IV.

At constant temperature it can be seen that the second term of equation (10) is a function of $c/(1 + A\sqrt{\Gamma})^2$, and the third term is a function of c. Therefore, at a given temperature

$$\bar{L}_2 = \nu z_1 z_2 L \frac{\sqrt{\Gamma}}{(1 + A\sqrt{\Gamma})} + \frac{Kc}{(1 + A\sqrt{\Gamma})^2} + K'c \qquad (12)$$

in which K and K' are constants.

The cell measures $\bar{H}_m - \bar{H}_{0.05}$ and not $\bar{L}_2$. Therefore, it is necessary to construct two equations at two concentrations at which $\bar{H}_m - \bar{H}_{0.05}$ has been measured and solve simultaneously for K and K'. In the present instance, the values of $\bar{H}_m - \bar{H}_{0.05}$ at 0.25 M and 1 M were substituted, and the constants obtained are given in Table V. With the use of these constants in equation (12), the values of $\bar{H}_{0.05} - \bar{H}_0$ were computed. From these and the values of $\bar{H}_m - \bar{H}_{0.05}$ calculated by equation (6) and smoothed by plotting against $m^{1/2}$, the values of $\bar{L}_2$ in the table were compiled.

TABLE V

RELATIVE PARTIAL HEAT CONTENT OF SODIUM HYDROXIDE: $\bar{L}_2 = \bar{H} - \bar{H}_0$ (CAL.)

m	0°	5°	10°	15°	20°	25°	30°	35°
0.05	− 7	22	50	80	108	137	167	200
.25	− 200	− 130	− 50	30	100	180	250	330
.5	− 390	− 305	−190	− 95	− 10	80	115	315
1	− 670	− 540	−410	−280	−160	− 20	130	270
1.5	− 810	− 670	−520	−360	−205	− 50	100	260
2	− 940	− 770	−615	−420	−240	− 80	100	300
2.5	−1060	− 870	−700	−460	−260	− 70	145	360
3	−1125	− 925	−730	−475	−260	− 35	200	430
3.5	−1175	− 980	−750	−485	−250	5	250	520
4	−1190	−1000	−795	−490	−240	50	310	600
$-K \times 10^{-3}$	3.26	3.02	2.22	1.54	1.24	0.934	0.485	0.014
$-K' \times 10^{-3}$	0.1	0.102	0.236	0.316	0.390	.277	.286	.330

As a check upon this computation of $\bar{H}_{0.05} - \bar{H}_0$, we have employed equation (9), and obtained 18, 100 and 180 cals. at 5, 20 and 35°, respectively. These results agree as well as expected with 22, 108 and 200 cal. obtained by the use of equation (12).

The final results are shown in Fig. 1 in which $\bar{L}_2$ is plotted against $m^{1/2}$ at 0, 20, 25 and 30°. The dotted line represents the values obtained by Rossini[7] from calorimetric data at 18° whence it is seen that good agreement has been obtained. The curves are of the same form as those obtained in the case of sodium chloride by Harned and Nims. This could be predicted by equation (10) and a knowledge of the temperature coefficients of a and B. The first term of this equation is positive. da/dT will be zero or nearly so. This will make the second term negative since y is negative and larger than the contribution due to the term containing the temperature coefficient of log Γ. Now, if dB/dT is positive and greater than dc/dT, which in all cases is negative above 5°, the third term of equation (10) will be negative. This state of affairs is true in the cases of sodium chloride and hydroxide solutions. If dB/dT is negative, as with hydrochloric acid solutions, then the third term of equation (10) will be positive, a fact previously discussed by Harned and Ehlers.

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[7] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

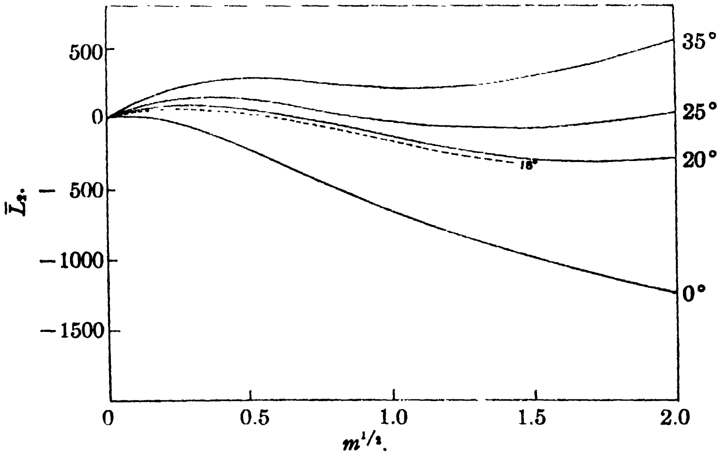

Fig. 1.—The relative partial molal heat content of sodium hydroxide in aqueous solution.

The peculiar tendency of the curves in Fig. 1 to bend upward in the concentrated solutions indicates that empirical equation (12) is not valid at concentrations above 1 M. An additional term such as Dc^n in the original Debye and Hückel equation for ln f should remedy this defect. Harned and Ehlers employed a term Dc^2 with success in their treatment of hydrochloric acid solutions. Since our data are not of as high accuracy as theirs, we have not resorted to this refinement. This discrepancy does not detract from the usefulness of equation (12) to determine $\bar{L}_2$ at some low reference concentration such as 0.05 M.

The Relative Partial Molal Heat Capacity of Sodium Hydroxide in Aqueous Solution.—$\bar{C}_p - \bar{C}_{p_0}$ was obtained in a manner similar to that described by Harned and Ehlers. For the cells in question, the relation between E and relative partial molal heat capacity is given by

$$\bar{C}_{p_0} - \bar{C}_p = NFT\frac{\partial^2 E}{\partial T^2} \quad (13)$$

From equation (2)

$$\partial^2 E/\partial T^2 = 2b \quad (14)$$

Hence

$$\bar{C}_p - \bar{C}_{p_0} = -NFT2b \quad (15)$$

The values of this quantity may be computed from the smoothed values of b, given by b' in Table I. If these are added to 6 cal., which is found to be the value of $\bar{C}_{p0.05} - \bar{C}_{p_0}$ from the slope of the plot of $\bar{H}_{0.05} - \bar{H}_0$ against T, $\bar{C}_p - \bar{C}_{p_0}$ may readily be obtained. The limiting equation of the Debye and Hückel theory can conveniently be expressed by

$$\bar{C}_p - \bar{C}_{p_0} = \nu z_1 z_2 Q \sqrt{\Gamma} \tag{16}$$

Values of Q from 0 to 60° were computed and are included in Table IV.

In Fig. 2, $\bar{C}_p - \bar{C}_{p_0}$ at 25° is plotted against $m^{1/2}$. The dotted line represents the results recently obtained by Gucker and Schminke[8] from calorimetric measurements from 0.04 to 2.5 M. The agreement is good when we consider that the maximum deviation is 2 cal., which occurs at 1 M. Our results also check those computed by Rossini to within a few calories.[9]

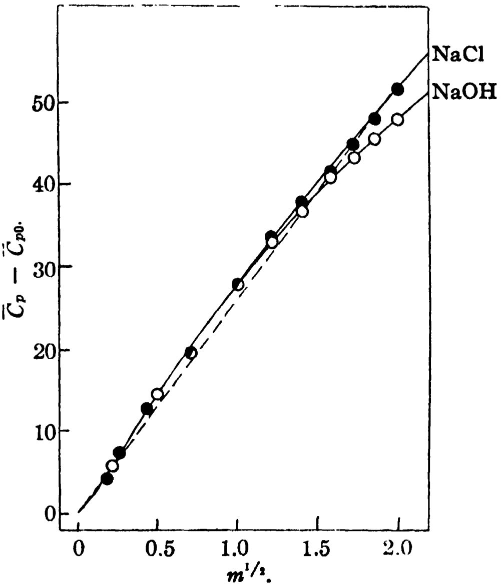

Fig. 2.—The relative partial molal specific heat of sodium hydroxide in aqueous solution at 25°.

$\bar{H} - \bar{H}_0$ and $\bar{C}_p - \bar{C}_{p_0}$ of Sodium Chloride from Electromotive Force Data.—We have previously mentioned that Harned and Nims in their investigation of sodium chloride solutions determined $\bar{H} - \bar{H}_{0.1}$ of this electrolyte but did not extrapolate their results to zero concentration. Further, they used a graphical method involving plots of first order differences of the electromotive forces against the temperature in order to obtain the constants of equation (2) and subsequently, $\bar{H} - \bar{H}_{0.1}$. Since our earlier computations did not agree with the calorimetric data so well as in the cases of sodium hydroxide and hydrochloric acid solutions, we have subjected the results to a recalculation by using the method of least squares for evaluation of a and b constants of equation (2). We found that the new values of $\bar{H} - \bar{H}_{0.1}$ derived therefrom did not differ sufficiently from those obtained by Harned and Nims to warrant a published revision. Our next step was to employ equation (12) in order to determine $\bar{L}_2$ at 0.1 M. The values of A employed were those given by Harned and Nims. Suffice to say that $\bar{H}_{0.1} - \bar{H}_0$ was found to be −88, −50, −10, 29, 68,

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(8) Gucker and Schminke, This Journal, 55, 1013 (1933).

(9) Rossini, *Bur. Standards J. Research*, 7, 47 (1931).

106, 146, 186 and 225 at 0, 5, 10, 15, 20, 25, 30, 35 and 40°, respectively. If these be added to the values given in Table III of Harned and Nims, $\overline{L}_2$ as measured from their electromotive forces may be computed. From the slope of the plot of $\overline{L}_2$ at 0.1 M against T, $\overline{C}_p - \overline{C}_{p_0}$ at this concentration is found to be 8 cals.

The agreement with calorimetric data is only fair. At 18° the results agree with values recently computed by Rossini to within ±30 cal., which is considered very good.[7,9] At 25°, our results do not check those recently computed by Robinson[10] nearly so well. They agree up to 0.5 M quite closely. Above this concentration, the difference increases until it reaches a maximum of 100 cal. at 1.5 M and then decreases to 50 cal. at 4 M. This maximum deviation corresponds to an error of approximately 0.01 mv. per degree in the temperature coefficient of electromotive force. In general, our values of $\overline{L}_2$ show a wider spread with temperature than those computed from the calorimetric data. This leads to higher values for $\overline{C}_p - \overline{C}_{p_0}$ than were found by Randall and Rossini.[11]

For the sake of comparison, we have reëvaluated $\overline{C}_p - \overline{C}_{p_0}$ by the method employed in the present communication. Thus, according to equation (15), we have

$$(\overline{C}_p - \overline{C}_{p_0}) = (\overline{C}_p - \overline{C}_{p_{0.1}}) + (\overline{C}_{p_{0.1}} - \overline{C}_{p_0}) = -NFT2b + 7.9 \qquad (17)$$

In Table VI are given the values of b and $\overline{C}_p - \overline{C}_{p_0}$ at 25° which latter are shown in Fig. 2 by inked-in circles. It is to be noted that these results are nearly the same as those for sodium hydroxide. As previously pointed out by Harned and Nims, the agreement with the values of Randall and Rossini is only fair.

TABLE VI

$(\overline{C}_p - \overline{C}_{p_0})_{25}$ OF SODIUM CHLORIDE

m	0.05	0.1	0.2	0.5	1	1.5	2	2.5	3	3.5	4
$(-b) \times 10^6$	−0.25	..	0.32	0.90	1.47	1.93	2.22	2.50	2.75	2.98	3.20
$(\overline{C}_p - \overline{C}_{p_0})$	4.5	7.9	12.3	20.3	28.1	34.4	38.4	42.3	45.7	48.9	51.9

Further Considerations.—The present investigation completes a series of results in which the hydrogen, silver–silver chloride and sodium amalgam electrodes have been combined with each other to form three separate cells from the measurements of which the thermodynamic properties of aqueous hydrochloric acid, sodium hydroxide and sodium chloride have been computed. The most important feature of results of this kind is the determination of the partial free energies and activity coefficients, since such determinations yield directly information regarding the fundamental parameters which are employed to express these quantities. When we attempt the determination of partial molal heat contents and heat capacities, we are subjecting the original data to a very severe test, since the

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(10) Robinson, THIS JOURNAL, 54, 1311 (1932).

(11) Randall and Rossini, *ibid.*, 51, 323 (1929).

determination of these quantities involves the first and second differential coefficients of the original results with the temperature. If our results agree with those determined by well conducted calorimetric measurements, we have reason to believe in the accuracy of the original electromotive forces as well as the calorimetric data. In matters of this sort, it is very important to obtain agreement by the use of entirely different experimental mechanisms.

Considering all the difficulties, both experimental and arithmetical, we regard the agreement so far obtained to be very encouraging, particularly in those cases when the amalgam electrode has been employed. This among other facts surely indicates that these measurements approach closely the cell mechanism which has been premised.

Summary

1. Measurements of the cells $H_2 | NaOH\ (m) | Na_xHg | NaOH\ (0.05) | H_2$ have been made from 0 to 35° at 5° intervals.

2. From these, activity coefficients, relative partial molal heat contents and heat capacities of sodium hydroxide from 0 to 35° have been computed. Good agreement has been obtained with calorimetric data.

3. A useful equation for the extrapolation of the partial molal heat content has been developed.

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A Study of the Cell, Pt/Quinhydrone, HCl (0.01 *M*)/AgCl/Ag, and the Normal Electrode Potential of the Quinhydrone Electrode from 0 to 40°[1]

BY HERBERT S. HARNED AND DONALD D. WRIGHT

Since its introduction in 1921, the quinhydrone electrode has found wide use as a convenient substitute for the hydrogen electrode in determining the *P*H of acid solutions, particularly in cases where the substances under examination are reduced by hydrogen in the presence of platinum black. However, in relatively few instances has it been employed in cells without liquid junctions, for the precise evaluation of thermodynamic data. Therefore, preliminary to using such cells in a determination of the dissociation constants of chloroacetic and other substituted acids, we found it necessary to study carefully the cell

$$\text{Pt/Quinhydrone, HCl } (m)\text{/AgCl/Ag} \qquad (I)$$

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[1] The material contained in this paper forms part of the dissertation presented to the Faculty of the Graduate School of Yale University by Donald D. Wright in June, 1933, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

in order to perfect a simple and reliable method of operation, employing vacuum technique, and to establish the limits of reproducibility. Our purpose also required that we obtain an accurate series of values of the electromotive force of this cell from 0 to 40°, when the molality of acid is 0.01 M. We shall combine these with data from the cell

$$H_2\,(1\text{ atm.})/HCl\,(m)/AgCl/Ag \qquad \text{(II)}$$

which was investigated by Harned and Ehlers,[2] employing a technique similar to ours. This procedure will give the normal potential of cell I and new values of the normal potential of the important cell

$$\text{Pt/Quinhydrone, HCl}\,(m)/H_2\,(1\text{ atm.}) \qquad \text{(III)}$$

which is the normal electrode potential of the quinhydrone electrode.

The fundamental equation for the calculations is

$$E = E_0 - \frac{2RT}{F}\ln \gamma m - \frac{RT}{2F}\ln \frac{a_{\text{Quinone}}}{a_{\text{Hydroquinone}}} \qquad (1)$$

which gives the electromotive force of cell I, corresponding to the cell reaction

$$\text{Hydroquinone} + 2\,AgCl = \text{Quinone} + 2\,HCl + 2\,Ag$$

The last term on the right side of this equation, which cannot be evaluated from the cell measurements alone, may be neglected in this case, as the solution is distinctly acidic and has a low ionic strength, and the quinhydrone employed is believed to have been free from an excess of either of its components.[3] Therefore, with the aid of activity coefficients of hydrochloric acid taken from the data of Harned and Ehlers, the measured values of E found at slightly varying molalities may be corrected to even molality, $m = 0.01$, and from the series of standard values so obtained, the normal potential, E_0, may be computed over the entire temperature range. Knowing the E_0 values for cell II, those for cell III follow by simple subtraction.

Materials and Apparatus

Quinhydrone.—As already pointed out, the quinhydrone used in electrode work should be free from any excess of either quinone or hydroquinone. There is a great diversity of opinion as to the best method of obtaining such a product.[4] Biilmann[5] believes that the crude crystals made by precipitation from an aqueous hydroquinone solution with ferric alum are suitable after simple washing with cold water and subsequent drying at room temperature. The difficulty in further purification lies in finding the proper solvent for recrystallization. In water and alkaline media there is danger of autoxidation of hydroquinone to quinone,[6] while the beautiful product obtained from acetic acid solution is always under suspicion of containing adsorbed acid. Because of the divergence of opinion, the following method was devised for this work, with a special view to avoiding autoxidation. Eastman product was recrystallized from boiled water at 70° in an atmosphere of nitrogen. The crystals which separated on cooling were filtered on a Büchner funnel, washed as far as possible in the absence of air, and dried at room temperature between filter papers. This product melted sharply at about 170°. It was stored in a brown glass-stoppered bottle. Certain investigators, such as Biilmann and Jensen,[7] have found it advisable to wash the quinhydrone just before use with some of the cell solution, in order to remove any excess hydroquinone left by slow evaporation of the quinone. This refinement was not adopted here, however, as being poorly suited to vacuum technique, but the dry quinhydrone was used directly from the bottle.

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[2] Harned and Ehlers, THIS JOURNAL, 54, 1350 (1932); 55, 2179 (1933).

[3] The last term may be divided into two parts, the logarithm of a concentration ratio and the logarithm of a ratio of activity coefficients. Since $K_1 = 10^{-10}$ and $K_2 < K_1$ for the ionization of hydroquinone (see p. 406 in Clark, "The Determination of Hydrogen Ions," 3rd ed., 1928, Williams and Wilkins Co., Baltimore) the molalities of quinone and hydroquinone are practically equal, and the concentration factor vanishes in solutions more acid than P_H 7, provided that the quinhydrone is pure. According to Hückel's equation, the activity coefficient factor equals $B\mu$, where μ is the ionic strength. The proportionality constant is small in the present instance, so that the term becomes negligible when $\mu = 0.01$.

[4] See pp. 410–411 in Clark, "The Determination of Hydrogen Ions," 3rd ed., 1928, Williams and Wilkins Co., Baltimore.

[5] Biilmann, *Bull. soc. chim.*, [4] 41, 213 (1927).

Hydrochloric Acid.—Stock solutions of approximately 0.01 *M* concentration were made from redistilled acid and analyzed gravimetrically. Their strengths were known to 0.3% or better.

Before the hydrochloric acid solution was run into the cells, it was boiled under reduced pressure to remove dissolved air, and then backed with nitrogen.[8] The loss in weight was assumed to be water. All weights were corrected to a vacuum basis.

Cell Technique.—The design and operation of a cell will be made clear by reference to Fig. 1. The quinhydrone electrode is represented by A, the silver–silver chloride electrode by B. Preliminary measurements had shown that because of diffusion of quinhydrone to the silver–silver chloride electrode, no equilibrium could be attained without complete separation of the two electrode compartments (D and E). Moreover, it was evident that there was no convenient means of washing solid quinhydrone with the cell solution when employing vacuum technique, while, on the other hand, washing was a necessity in the case of the silver–silver chloride electrode. Therefore, it was decided to interpose the 3 mm. stopcock, C, and 7 to 8 cm. of 3 mm. capillary tubing between the electrode compartments, D and E, and connect the outlets to air, vacuum and solution (F) and waste (I) all to the silver–silver chloride side of the cell, so that, first, the silver–silver chloride electrode could be rinsed completely without wetting the quinhydrone side, D, second, both D and E could then be evacuated and filled simultaneously, and, finally, the solution in compartment D could be separated from that in E except at the moment of reading the electromotive force. At point F, the upper tube divided into two branches, one through the stopcock G, leading to the solution flask and the other through the stopcock, H, leading to the vacuum and air lines. The cell was held in

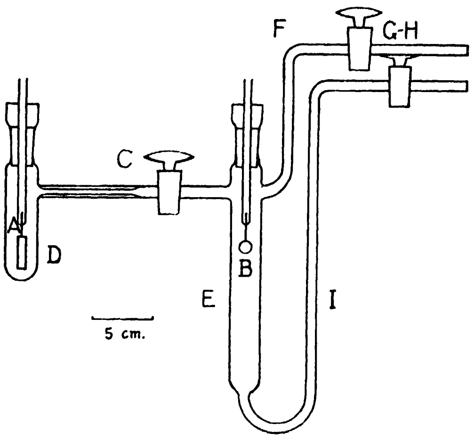

Fig. 1.—The cell.

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(6) La Mer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923); La Mer and Rideal, THIS JOURNAL, **46**, 223 (1924).

(7) Biilmann and Jensen, *Bull. soc. chim.*, [4] **41**, 151 (1927).

(8) Hydrogen is unsuitable for this purpose, as it quickly diffuses through the solution and causes measurable reduction of the quinhydrone. This is a possible source of error in the direct use of cell III.

place in the thermostat by a rack and connected to the solution flask and the air-vacuum-waste manifolds by short pieces of pressure tubing.

The operation of filling the cell proceeded as follows: the cell, previously rinsed with water, distilled water, and redistilled alcohol, and dried, was put in place in the thermostat, a quantity of quinhydrone was dropped to the bottom of compartment D sufficient to saturate the solution in that compartment, and the two electrodes, A and B, were inserted. Then stopcock C was closed and compartment E evacuated with the water pump and rinsed completely with the solution. The solution was sucked out through I into the waste flask, the necessary air being admitted through H. E was then re-evacuated and rinsed with solution to a level above that of the silver–silver chloride electrode. When this solution had been sucked out, stopcock C was opened and the whole cell evacuated and finally filled completely with solution for the run. It is recognized that the evacuation process is open to the theoretical objection that it might alter the composition of the quinhydrone by volatilization of some quinone, but it is difficult to see how this disadvantage can be dissociated from the vacuum technique which has been shown to be necessary with the silver–silver chloride electrode.[9]

Between runs the platinum foil electrodes (2.5 × 0.5 cm.) were kept immersed in a dichromate cleaning mixture, after the method of Morgan, Lammert and Campbell,[10] and before use they were thoroughly rinsed with water, distilled water, and redistilled alcohol, and dried in a current of clean, dry air. The silver–silver chloride electrodes were those described as Type 2, by Harned.[11] They were made one day in advance of use and kept in distilled water until needed. Rinsing them with the cell solution before inserting them in the cells was found to add little, if anything, to the reproducibility attained.

The temperature of the water thermostat, which was read from a calibrated thermometer, generally remained constant to ±0.02°, both with ice and with electric heating. The electromotive forces were read upon a Leeds and Northrup Type K potentiometer with a high sensitivity galvanometer. Owing to the high internal resistance of the cells, the fifth decimal place in volts could in most cases only be estimated by interpolation. However, since the estimate was generally good to two or three hundredths of a millivolt, and several readings were included in the reported average, the averaged readings could justifiably be expressed to hundredths of a millivolt.

Experimental Results with the Cell, Pt/Quinhydrone, HCl (0.01)/AgCl/Ag.—Since our measurements were made with a somewhat different technique than hitherto employed with the quinhydrone and silver–silver chloride electrodes, it was thought necessary to make a sufficient number of runs to show definitely the reproducibility of the cell, and the limits of time during which equilibrium could be considered as established. Although, under some conditions, the quinhydrone electrode reaches equilibrium almost immediately[5] and is extremely reproducible,[10,12] this could not necessarily be expected to hold in our case. The reproducibility was studied by running each day four cells filled with the same solution. They were started at a definite temperature and the electromotive force was read until equilibrium apparently had been reached. Then the temperature was raised and the process repeated several times. When the readings finally began to drift noticeably, the run was stopped. Enough runs were made so that at least one was started fresh at each temperature reported.

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[9] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[10] Morgan, Lammert and Campbell, THIS JOURNAL, **53**, 454 (1931).

[11] Harned, *ibid.*, **51**, 416 (1929).

[12] Morgan and Lammert, *ibid.*, **53**, 2154 (1931); Lammert and Morgan, *ibid.*, **54**, 910 (1932).

Careful scrutiny of all the cell measurements first leads to the following conclusions. (1) In the particular type of cell employed, the time required to reach equilibrium varies from three hours at 0° to thirty to forty-five minutes at 25° and higher temperatures. (2) At low temperatures the cell is very difficult to read, both because of its high internal resistance and because of polarization of the quinhydrone electrode. (3) For unknown reasons, some cells do not reach equilibrium within a reasonable time. (4) While at low temperatures the electromotive force first decreases with the time, in nearly all cases it eventually begins to rise.[13] The rate of this rise varies with the individual cell, but it always increases with temperature and becomes quite pronounced above 25°. Consideration of equation (1) shows that this drift corresponds to an increase in the activity of hydroquinone or a decrease in the activity of quinone or of hydrochloric acid. It has long been known that quinone and concentrated hydrochloric acid react to form chlorohydroquinone,[14] and it therefore seems justifiable to ascribe the cause of the drift to this reaction, even at the low concentration of hydrochloric acid present in our cells.

In view of these conclusions, it was deemed best to report as the final value of the electromotive force, E_m, for a single run, the mean of all the readings for the four cells, excluding those values in which equilibrium had not yet been reached and completely excluding those cells which showed too rapid a drift in voltage and those which differed consistently from the others in their set by several tenths of a millivolt. About 8% of the cells were rejected. The deviations from the mean were calculated and used as a test of reproducibility, bearing in mind the number of readings excluded, if any.

The data thus obtained are given in Table I. This table contains, first, the mean values of the electromotive force of cell I at different temperatures and molalities, each run being reported separately, and, next, data on the reproducibility of this cell. The maximum and average deviations are deviations from the mean of those readings included in it. In column 8 are found values of $E_{0.01}$, the electromotive force at even molality m = 0.01, which were computed from E_m with the aid of equation (1). The runs are arranged in the table, at each temperature, according to the length of the time interval between filling the cell and commencing the readings, the run in which this time was shortest being placed first. No readings were made until thirty minutes had elapsed; in some cases they were reported up to ten hours. It is evident that the maximum and average deviations are not functions of the time, but rather of the tempera-

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(13) This rise may also be observed in the data of Biilmann, *Ann. chim.*, [9] **15**, 109 (1921).

(14) Wöhler, *Ann.*, **51**, 155 (1844).

TABLE I

ELECTROMOTIVE FORCES OF CELL I FROM 0 TO 40°, WITH DATA ON ITS REPRODUCIBILITY AND VALUES OF THE ELECTROMOTIVE FORCE CORRECTED TO 0.01 *M* CONCENTRATION

Temp., °C.	*m*	Mean E_m	E. m. f. values Included in mean	E. m. f. values Excluded from mean	Max. dev., mv.	Av. dev., mv.	$E_{0.01}$ (obs.)	$E_{0.01}$ (calcd.)	ΔE, mv.
0.18	0.01003	−0.26007	18	6	0.18	0.09	−0.25993	−0.25992	−0.01
10.00	.01003	− .24998	16	0	.10	.03	− .24983	− .24982	− .01
	.01003	− .24997	12	0	.15	.10	− .24982		.00
15.00	.01003	− .24495	11	2	.06	.03	− .24480	− .24490	+ .10
	.00986	− .24421	4	0	.11	.08	− .24487		+ .03
15.04	.01003	− .24502	8	0	.16	.08	− .24487	− .24486	− .01
20.00	.01003	− .24022	10	2	.12	.07	− .24007	− .24012	+ .05
	.00986	− .23950	13^a	0^a	.15	.09	− .24017		− .05
	.00986	− .23956	8	0	.10	.05	− .24023		− .11
	.01003	− .24028	8	0	.06	.04	− .24013		− .01
25.00	.01009	− .23598	14^a	1^a	.10	.03	− .23554	− .23549	− .05
	.01009	− .23602	6^b	0^b	.07	.03	− .23558		− .09
	.01003	− .23546	8	0	.07	.04	− .23530		+ .19
	.00986	− .23484	9^a	0^a	.06	.03	− .23552		− .03
	.01009	− .23604	12	0	.11	.05	− .23560		− .11
	.01003	− .23555	7	1	.06	.04	− .23539		+ .10
	.00986	− .23477	4	0	.11	.06	− .23545		+ .04
30.00	.01010	− .23153	15	0	.11	.05	− .23103	− .23101	− .02
	.01009	− .23141	15^b	0^b	.16	.05	− .23096		+ .05
	.01009	− .23138	12^a	0^a	.07	.03	(− .23093)		(+ .08)
	.00986	− .23024	6^a	0^a	.07	.04	(− .23093)		(+ .08)
	.01003	− .23088	8	0	.09	.04	(− .23072)		(+ .29)
	.01003	− .23104	8	0	.14	.09	(− .23088)		(+ .13)
35.00	.01009	− .22721	7^a	3^a	.06	.04	− .22675	− .22667	− .08
	.01010	− .22708	8	0	.09	.04	(− .22657)		(+ .10)
	.01009	− .22691	6^c	0^c	.08	.03	(− .22645)		(+ .22)
39.94	.01009	− .22291	6^a	0^a	.05	.03	− .22245	− 22253	+ .08
40.00	.01011	− .22309	20	7	.15	.06	− .22252	− 22248	− .04
	.01010	− .22275	12	0	.12	.05	(− .22223)		(+ .25)

[a] Values from three cells only. One cell completely excluded. [b] Values from three cells only. [c] Values from two cells only. Two cells completely excluded.

ture, being least in the middle range from 25 to 35°. The mean values of $E_{0.01}$, however, show a consistent rise with time at 30, 35 and 40°, as would be expected from the previous discussion. At 40° the readings generally become unreliable within three hours, and we consider that temperature to be the upper limit for precise work of this nature.

In order to find an analytic expression for $E_{0.01}$ as a function of temperature, taking into account this drift, all values were assigned equal weight except the bracketed ones, which were given no weight at all, and the method of least squares applied, assuming an equation of the form, $E = a + b(t - 25) + c(t - 25)^2$. The solution was

$$E_{0.01} = -0.23549_0 + 0.0009112_3(t - 25) - 2.939_1 \times 10^{-6}(t - 25)^2 \quad (2)$$

Values of $E_{0.01}$ calculated by means of this equation are given in the next to the last column of Table I, with the residual, or deviation between calculated and observed values, given in the last column.

We believe that the variations represented by the maximum and average deviations are inherent in this cell, and that an attempt to reduce them would render the technique too involved for general use. On the other hand, the discrepancies between the various runs, represented by ΔE, could doubtless be reduced by more precise analytical work and more uniform manipulation. We consider the present values from equation (2) accurate to within 0.1 mv. from 0 to 25° and to 0.15 mv. from 30 to 40°.

Normal Potentials.—From the values of $E_{0.01}$ computed at different temperatures by means of equation (2), the normal potential of cell I may be found by substituting in equation (1). It is important to note, however, that the values of E_0 obtained for this cell, cell II, and all other cells in which the electrolytes take part in the cell reactions, and the values of the activity coefficients of these electrolytes, are directly dependent on the choice of numerical values for the factor $k = 2.3026\ RT/F$, and for the Debye–Hückel limiting slope also, if we use Hitchcock's extrapolation.(15) We have therefore carried our calculations through in two ways: (a) using the values $k = 0.00019844T$ and $T = t + 273.1$;(16) in conformity with the choice of Harned and Ehlers,(17) and (b) employing the more recent values of Birge,(18) according to which $k = 0.00019848_5T$ and $T = t + 273.18$.

For method (a), E_0 for cell II is given by the least square equation of Harned and Ehlers

$$E_0 = 0.22239 - 645.52 \times 10^{-6}(t - 25) - 3.284 \times 10^{-6}(t - 25)^2 + 9.948 \times 10^{-9}(t - 24)^3 \quad (3a)$$

To obtain this quantity for method (b), it was necessary to perform a new extrapolation from the original electromotive force data of Harned and Ehlers. This was done from 0 to 40°, starting with their electromotive forces at round concentrations and using Hitchcock's method of extrapolation,(19) with Birge's values of the fundamental constants and Wyman's dielectric constants. The results, which are presented in the second column of Table II, are reproduced over the temperature range 0 to 40° by the least square equation

$$E_0 = 0.22223_1 - 644.80 \times 10^{-6}(t - 25) - 3.300 \times 10^{-6}(t - 25)^2 \quad (3b)$$

with a maximum deviation of 0.03 mv.

Then E_0 for cell I was calculated, first by method (a), using the activity coefficients evaluated by Harned and Ehlers from equation (3a) and their equation (9), and then by method (b), with activity coefficients found from equation (3b) and their equation (9). The observed values are set forth in

(15) This choice has virtually no effect on the correction of E_m to $E_{0.01}$. The activity coefficients employed in this calculation were those mentioned below under method (a).

(16) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

(17) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933). The values of the Debye–Hückel constant given by these authors were calculated from "International Critical Tables" data and the dielectric constants of Wyman, *Phys. Rev.*, **35**, 623 (1930).

(18) Birge, *Phys. Rev. Supplement*, 1, 1 (1929).

(19) Hitchcock, THIS JOURNAL, **50**, 2076 (1928).

TABLE II

NORMAL POTENTIALS OF CELLS I, II AND III FROM 0 TO 40°

t	E_0 − IIb (obs.)	E_0 − Ia (obs.)	E_0 − Ib (obs.)	E_0 − IIIb (Eq. 5b)
0	0.23627	−0.48156	−0.48160	−0.71790
5	.23384	− .48038	− .48048	− .71429
10	.23116	− .47936	− .47952	− .71066
15	.22833	− .47851	− .47867	− .70702
18				− .70482
20	.22537	− .47780	− .47799	− .70336
25	.22223	− .47728	− .47744	− .69969
30	.21894	− .47691	− .47707	− .69600
35	.21544	− .47668	− .47684	− .69230
40	.21182	− .47660	− .47678	− .68858

the third and fourth columns, respectively, of Table II. The two sets were least squared to give the equations

$$E_0 = -0.47727_5 + 91.83 \times 10^{-6}(t - 25) - 3.174 \times 10^{-6}(t - 25)^2 \qquad (4a)$$

$$E_0 = -0.47745_6 + 91.02 \times 10^{-6}(t - 25) - 3.008 \times 10^{-6}(t - 25)^2 \qquad (4b)$$

which fit all the data with a maximum deviation of 0.02 mv.

E_0 for cell III may be found either by subtracting (3a) from (4a), or (3b) from (4b), or by subtracting Harned and Ehlers' equation (9)

$$E_{0.01} = 0.46418 + 173.84 \times 10^{-6}(t - 25) - 3.11 \times 10^{-6}(t - 25)^2 + 7.00 \times 10^{-9}(t - 25)^3$$

which gives the electromotive force of cell II at 0.01 M concentration, from our equation (2). Since the three resulting equations give almost identical values, we shall present only the second, namely

$$E_0 = -0.69968_7 + 735.82 \times 10^{-6}(t - 25) + 0.292 \times 10^{-6}(t - 25)^2 \qquad (5b)$$

Values calculated from it are found in the last column of Table II.

These figures may be compared with those from two other sources. Biilmann and Jensen[7] measured cell III directly at 0.01 N concentration of hydrochloric acid and obtained for E_0 the value −0.70479 ± 0.00002 volts at 18°, which is in very satisfactory agreement with our result. Biilmann and Krarup[20] measured the same cell at 0, 18, 25 and 37.5°, employing 0.1 N HCl, 0.1 N HCl + 0.09 N KCl, and a phosphate buffer as electrolytes. All their results could be reproduced by the equation, $E_0 = -0.7175 + 0.00074t$ to within 0.4 mv. Correcting from the measurements of Biilmann and Jensen at 18° for the difference between these cells and the 0.01 N HCl cell, we obtain

$$E_0 = -0.7181 + 0.00074t \qquad (6)$$

Values calculated from this equation agree with those of Table II to 0.2 mv. or less. While the normal electrode potential of the quinhydrone electrode can undoubtedly be found most accurately by the direct measurement of cell III, in view of the number and character of the present meas-

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(20) Biilmann and Krarup, *J. Chem. Soc.*, **125**, 1954 (1924).

urements, we consider the values given in Table II to be the best available at this time.

Summary

1. A simple and reliable procedure has been described whereby the quinhydrone electrode may be used in cells without liquid junction, employing vacuum technique.

2. The reproducibility of the quinhydrone electrode in 0.01 *M* hydrochloric acid solution has been carefully studied, employing the cell Pt/quinhydrone, HCl (0.01 *M*)/AgCl/Ag. The electromotive force of this cell has been found to be reproducible to within a tenth of a millivolt from 0 to 40°, although side reactions destroy the equilibrium after a short time at temperatures above 30°.

3. Values have been obtained from 0 to 40° for the potential of the above cell and the normal potentials of that cell and the cell, Pt/quinhydrone, HCl/H_2, with an accuracy of ± 0.1 mv. from 0 to 25° and ± 0.15 mv. from 30 to 40°.

NEW HAVEN, CONNECTICUT RECEIVED AUGUST 19, 1933
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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE COLLEGE OF WASHINGTON]

The Activity Coefficients and Transference Numbers of Potassium Iodide[1]

BY RALPH W. GELBACH

Electromotive forces of concentration cells, with and without ion transfer, have been measured at 25 ± 0.02°. The following types of cells have been measured.

(A) KHg_x | KI m_1, AgI | Ag—Ag | AgI, KI m_2 | KHg_x
(B) KHg_x | KI m_1 | KI m_2 | KHg_x
(C) Ag | AgI, KI m_1 | KI m_2, AgI | Ag

Materials, Apparatus and Method.—Chemically pure potassium iodide was thrice recrystallized from distilled water and dried in an air-bath at about 80°. Solutions were made from weighed portions of the salt by adding a definite quantity of conductivity water and boiling for a definite time on an electric hot plate. The hot solutions were saturated with hydrogen by permitting the gas to bubble through them for several minutes, then finally cooled to room temperature under an atmosphere of hydrogen. By standardization of operations it was easily possible to control concentrations within 0.2%.

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(1) A portion of the data was obtained by Helen Marburger Fredell as a partial fulfilment for the Master's Degree.

The mercury used for making the amalgams was purified as previously described.[2]

The amalgam was prepared by electrolyzing a solution of chemically pure potassium hydroxide. The concentration of potassium was about 0.1%.

The apparatus was the same as used previously.[3]

The silver iodide electrodes were prepared in a manner similar to the preparation of the silver bromide electrodes.[3] These deviated among themselves by not more than 0.03 millivolt.

In Table I are given the electromotive forces of the concentration cells with and without liquid junction. The value given in each case is the mean of at least two separate sets of readings. Due to instabilities of the system the accuracy of duplication is less than desired, the maximum deviation in some cases being slightly in excess of 0.5%.

TABLE I

m_1	m_2	E_A, volt	$E_{comp.}$, volt	ΔE, mv.	E_B, volt	E_C, volt	$E_{comp.}$, volt	ΔE, mv.
0.002	0.020	0.11153	0.1137	2.2	0.05585	0.05552	0.05623	0.71
.005	.050	.11083	.1118	1.0	.05492	.05523	.05537	.14
.010	.050	.07622	.0777	1.5	.03800	.03671	.03821	.60
.010	.100	.10925	.1105	1.3	.05524	.05414	.05448	.34
.020	.100	.07653	.0767	0.2	.03879	.03769	.03770	.01
.020	.200	.10872	.1092	.5	.05512	.05365	.05363	− .02
.050	.500	.10817	.1082	.0	.05514	.05322	.05319	− .03
.050[a]	.500	.1087	.1082	.5				
.100[a]	1.000	.1091	.1091	.0				
.200[a]	2.000	.1125	.1125	.0				

[a] Data from Harned and Douglas.

Activity coefficients were calculated in a manner similar to that used by Scatchard.[4] In consequence of the measurements having been made on concentration cells only an arbitrary value of 2 volts was assumed for the electromotive force of the cell KHg_x/KI 0.01 m, AgI/Ag. On this basis values of E_0' have been calculated.

In very dilute solution $E_0 - E_0' = -0.05915\sqrt{m}$ which upon differentiation with respect to $\sqrt{m}$ gives a slope at zero concentration of 0.05915. By plotting the values of E_0' against $\sqrt{m}$ and extending the curve to infinite dilution so that the slope at the intercept of the zero axis was 0.05915 the value of E_0 was found to be 1.7591 volts. The activity coefficients calculated from the equation

$$E_0' = E + 0.1183 \log m = E_0 - 0.1183 \log \gamma \qquad (1)$$

are shown in column 4 of Table II.

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(2) Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1023 (1925).

(3) Gelbach and Huppke, THIS JOURNAL, **48**, 1504 (1926).

(4) Scatchard, *ibid.*, **47**, 641 (1925).

TABLE II

m	E	E_0'	γ	γ_{calcd}	$\gamma_{\text{H\&D}}$	N_{K}
0.002	2.07881	1.75952	0.992	0.952		0.4983
.005	2.03461	1.76240	.938	.928		.4979
.010	2.00000	1.76340	.920	.903		.4974
.020	1.96728	1.76629	.869	.872		.4968
.050	1.92378	1.76987	.810	.820		.4954
.100	1.89075	1.77245	.772	.775	0.775	.4940
.200	1.85856	1.77587	.721	.719		.4917
.300	1.8386	1.7768	.709	.703	.715	
.500	1.81561	1.7800	.666	.674		.4878
.500[a]	1.8150	1.7796	.674	.674	.678	
1.000[a]	1.7816	1.7716	.645	.648	.649	
2.000[a]	1.7461	1.7817	.644	.651	.646?	

[a] These voltages are from "corrected" electromotive force data of Harned and Douglas, THIS JOURNAL, 48, 3095 (1926).

The Debye–Hückel constants were evaluated by substituting in the equation

$$\log \gamma = \frac{-0.354\sqrt{2m}}{1 + N\sqrt{2m}} + P\,(2m) \tag{2}$$

values of γ at several concentrations. A graphic solution of this system of equations yielded approximate values of N and P which were used as first approximations in the equation

$$E_2 - E_1 = \frac{4.605\,RT}{F}\left[\frac{0.354\sqrt{2m_1}}{1 + N\sqrt{2m_1}} - \frac{0.354\sqrt{2m_2}}{1 + N\sqrt{2m_2}} + 2P\,(m_2 - m_1) + \log\frac{m_2}{m_1}\right] \tag{3}$$

In a manner similar to that of Jones and Dole[5] N and P were determined to be, respectively, 0.866 and 0.0182. Observed and computed electromotive forces for cells without transference are shown in columns 3 and 4 of Table I. The agreement is satisfactory in concentrations greater than 0.01 molal but at higher dilutions the deviation becomes as large as 2%, which, in all probability, is largely due to difficulties encountered with the amalgam electrodes.

The activity coefficients calculated from equation (2) which are shown in column 5 of Table II are considered to be more accurate than those determined by the extrapolation method because of the unreliability of data obtained with amalgam electrodes in dilute solution. These values also correlate much better those given by Harned and Douglas (*loc. cit.*).

Transference numbers were calculated from the equation of Jones and Dole,[5] $t = A/(1 + B\sqrt{m})$. The equation for the electromotive force, E_t, of the cell, type C, was employed for the evaluation of the constants A and B. Substituting $A = 1.4990$ and $B = 0.0106$, the computed values of E_t show very good agreement with the observed voltages. Referring to columns 8 and 9, it is to be noted that agreement here is much better

(5) Jones and Dole, THIS JOURNAL, 51, 1073 (1929).

$$E_t = \frac{2RT}{F}\left[(1 - A)\ln\frac{m_2}{m_1} + A\ln\frac{1 + B\sqrt{m_2}}{1 + B\sqrt{m_1}} + \left[\frac{0.8152}{N} + \frac{1.153\,A}{B - N\sqrt{2}}\right] \times \left[\frac{1}{1 + N\sqrt{2m_2}} - \frac{1}{1 + N\sqrt{2m_1}}\right] + \frac{1.153\,AB}{(B - N\sqrt{2})^2}\left[\ln\frac{1 + B\sqrt{m_2}}{1 + B\sqrt{m_1}} + \ln\frac{1 + N\sqrt{2m_2}}{1 + N\sqrt{2m_1}}\right] + 4.6052\,P(m_2 - m_1) - \frac{9.2103\,AP}{B^2}\left[B\sqrt{m_2} - B\sqrt{m_1} - \ln\frac{1 + B\sqrt{m_2}}{1 + B\sqrt{m_1}}\right]\right] \quad (4)$$

than in the case of the amalgam electrodes. Even though errors are rather large in higher dilutions, the constants are sufficiently well defined to render transference numbers accurate beyond the third decimal place as they were formerly expressed.

Summary

1. The electromotive forces of concentration cells of potassium iodide have been measured.

2. The Debye–Hückel constants have been determined for potassium iodide and the activity coefficients have been calculated.

3. Transference numbers have been accurately determined.

PULLMAN, WASHINGTON

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Intermediate States of Reduction of Chromic Acid[1]

BY T. R. BALL AND KEITH D. CRANE

Weinland and his co-workers[2] have prepared several double salts of pentavalent chromium oxychloride, $CrOCl_3$, with the chlorides of the alkali metals and with the hydrochlorides of organic bases.[3] Olsson[4] has repeated this work and also prepared a double fluoride of CrO_2F with potassium fluoride. A search of the literature has failed to reveal the isolation of any other pentavalent chromium compounds. However, a number of authors have postulated the intermediate formation of penta- and tetravalent chromium in the reduction of chromic acid.[5] This has

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(1) This work was made possible by assistance to the senior author from a grant made by the Rockefeller Foundation to Washington University for research in science.

(2) Weinland, *Ber.*, **37**, 3784 (1905); Weinland and Fiederer, *ibid.*, **39**, 4042 (1906); **40**, 2090 (1907).

(3) Weinland and Beck, "Darstellung anorganischer Präparate," J. C. B. Mohr, Tübingen, 1913, p. 97.

(4) Olsson, *Arkiv. Kemi. Mineral Geol.*, **9**, No. 10, 10 (1924).

(5) Bray, *Z. physik. Chem.*, **54**, 463 (1906); Luther and Rutter, *Z. anorg. Chem.*, **54**, 1 (1907); Jabłczyński, *ibid.*, **60**, 38 (1908); Mitchell, *J. Chem. Soc.*, **125**, 564 (1925); Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1931, 2d ed., p. 275.

been done to explain reaction velocities or induction factors. Bohle[6] found that the reduction of chromic acid by ferrous sulfate in the presence of hydriodic acid resulted in the induced liberation of iodine in quantities that could be accounted for by the formation of pentavalent chromium sulfate as an intermediate stage in the reduction. Assuming that the reaction between pentavalent chromium and hydriodic acid is fast, there should be two equivalents of iodine liberated for each mole of ferrous sulfate added, as the following equations show

$$2FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = Fe_2(SO_4)_3 + Cr_2(SO_4)_5 + K_2SO_4 + 7H_2O$$
$$Cr_2(SO_4)_5 + 4HI = Cr_2(SO_4)_3 + 2H_2SO_4 + 2I_2$$

Induction factors approaching 2 were found.

Manchot[7] offers an alternative theory involving the initial oxidation of the iron to the pentavalent state. This would also account for an induction factor of 2 through the following stages

$$2FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = Fe_2(SO_4)_5 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$
$$Fe_2(SO_4)_5 + 4HI = Fe_2(SO_4)_3 + 2H_2SO_4 + 2I_2$$

The data available prior to the present investigation do not prove either of the above mechanisms. It seemed advisable, therefore, to investigate the reduction of chromic acid by ferrous sulfate and other reducing agents by the Allison[8] magneto-optic method. The positions of the minima in this method are a function of the equivalent weights of the cations and are also dependent upon the anion. The method is, therefore, admirably suited to the detection of intermediate stages in chemical reactions. Working in the sulfate series, the minima for $Cr_2(SO_4)_5$ (equiv. wt., 58.42) and for $Fe_2(SO_4)_5$ (equiv. wt., 59.18) should fall between those of $Al_2(SO_4)_3$ and $MgSO_4$ whose minima occur at 9.66 and at 10.04, 10.40 and 10.62, respectively. The last three minima are characteristic of the three isotopes of magnesium as sulfates. At the present stage of development of the method, it is not possible to distinguish between two compounds whose equivalent weights are as close together as those of pentavalent chromium and iron sulfates by the position of the minima unless the compounds could be isolated in the pure state. However, it is possible to distinguish them by depending upon the fact that iron and chromium salts exhibit two and four minima, respectively. In the data which follow, it will be shown that four minima are observed in the range appropriate to pentavalent chromium sulfate and that it is an intermediate in the reduction of chromic acid with four different reducing agents.

Experimental

General Procedure.—All of the chemicals used were of the highest purity available from commercial sources. The water was redistilled from an all glass Pyrex still equipped with two Kjeldahl traps in series.

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[6] Bohle, Thesis for the M.S. degree at Washington University, 1931.

[7] Mancnot, *Ann.*, 325, 165 (1902).

[8] Allison and Murphy, THIS JOURNAL, 52, 3796 (1930).

Standard ferrous and mercurous sulfates were prepared in 5% sulfuric acid and the stannous chloride in concentrated hydrochloric acid. Oxalic acid was prepared in aqueous solution.

Ten ml. of 0.10 *N* potassium dichromate was added to about 500 ml. of water acidified with sulfuric acid. The reducing agent was added dropwise with constant stirring in such quantities as to leave the dichromate in 10% excess and the solution was examined at once for intermediate oxidation-reduction products. Each reducing agent and the dichromate was tested separately for minima in the critical ranges to be studied and showed no minima in these regions of the scale.

Results.—Table I shows the data obtained using four different reducing agents. The first column shows the reducing agent used and the second the number of independent mixtures which were examined. The total number of minima observed are listed in the third column and their position in the fourth column. Each of the mixtures was observed at various intervals to get information as to the persistence of the intermediate compound. The approximate time of the disappearance of the minima is given in the last column.

TABLE I

POSITIONS OF THE MINIMA OF THE INTERMEDIATE REDUCTION COMPOUNDS OF CHROMIC ACID

Reducing agent	No. of mixtures examined	Total no. of rdgs.	Positions of minima				Persistence of minima
$FeSO_4$	6	121	9.73	9.80	9.86	9.92	46–60 hours
$H_2C_2O_4$	4	256	9.73	9.80	9.86	9.93	21–42 days
Hg_2SO_4	2	212	9.73	9.80	9.86	9.92	10–15 days
$SnCl_2$	3	26	9.73	9.80	9.86	9.91	1.5–4 hours
	Total readings	615					

Figure 1 contains a compilation of all the minima observed with all the reducing agents listed in Table I. The scale readings are plotted against the number of times each minimum was observed. The curve is a summation of the individual curves for each reducing agent. The positions of the peaks on the composite curve fall, within the limits of experimental error, at the same points as on the individual curves from which the positions of the minima in Table I are deduced.

A total of 615 minima were observed, 93.4% of which fall within 0.02 scale division (3 mm.) of some peak and 31% fall on a peak. The uniform distribution of the readings on either side of the peaks places the minima at 9.73, 9.80, 9.86 and 9.92. These occur in the range between aluminum and magnesium sulfates and show the presence of some compound of intermediate equivalent weight. Since there are four distinct minima they are attributed to pentavalent chromium sulfate.

Ball and Bohle(9) in a study of the induced reaction between chromic and hydriodic acids, using ferrous sulfate as the inductor, at first postulated the formation of pentavalent chromium. But in a brief preliminary study by the magneto-optic method only two minima were observed at 9.72 and 9.80. From these data the induced reaction was attributed to pentavalent iron, confirming the hypothesis of Manchot. In the above paper by Ball and Bohle this explanation was given. However, in view of the present more complete investigation, we believe that this conclusion was erroneous, since four minima were observed in the case of all reductants, three of which contained no iron.

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(9) Ball and Bohle, Washington University Studies, New Ser., *Science and Technology*, No. 6, 82 (1932).

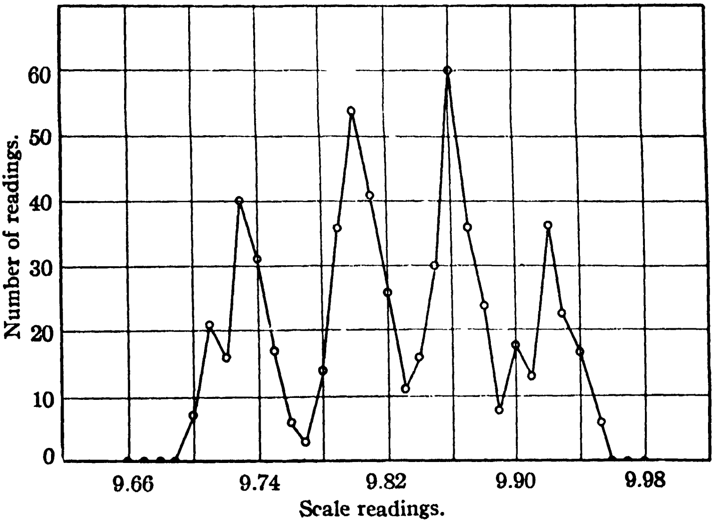

Fig. 1.—Distribution of scale readings.

Discussion

In the solutions, after mixing, there would be present potassium and chromic ions as well as the oxidized form of the metallic ion added as reductant. There would also be present, sulfate, chromate and dichromate ions, and chloride ions in the case of stannous chloride. It might be assumed that the four minima which appeared as a result of the reaction are due to salts formed between some of the above ions. This possibility is precluded by the fact that the minima disappear after some time, indicating an unstable compound. Moreover, we have found that chromic acid gives minima at 6.03 and 6.13, sodium chromate at 7.52, 7.65 and 7.77, and potassium chromate at 8.38 and 8.58. Since the equivalent weight of chromic chromate, $Cr_2(CrO_4)_3$, which is common to all the solutions, is between that of chromic acid and sodium chromate, its minima should fall between 6.13 and 7.52. Chromic sulfate minima occur at 11.15, 11.24, 11.35 and 11.45. These salts are therefore precluded as sources of the four minima observed. Calculations based upon the equivalent weights of the sulfates, chromates and dichromates of all the other positive ions, such as mercuric, stannic and ferric, preclude these from this range.

Mitchell[10] has assumed that an acid, $H_2Cr_2O_6$, containing pentavalent chromium is formed in the reduction of chromic acid by hypophosphorous acid and that it is rapidly reduced by excess of hypophosphorous acid, possibly passing through a tetravalent state. If such an acid is formed, it would have a higher equivalent weight than chromic acid, H_2CrO_4, and its minima would fall below those of the latter acid. Similarly, the minima of its chromic salt would fall below those of chromic chromate which has already been calculated to fall below 7.52 on the scale. Therefore it is concluded that the minima observed at 9.73, 9.80, 9.86 and 9.92 in all solutions, are those of pentavalent chromium sulfate.

It is highly probable that tetravalent chromium may be a step in the reduction, but a search of the scale in its possible range failed to yield any evidence of its presence in any of the solutions. A further study with other reducing agents might yield positive results.

In the case of stannous chloride, eleven minima were observed in the range about midway between those of stannous and stannic chlorides. These were observed when the stannous chloride was in excess of that required for the complete reduction of the chromic acid and were never observed when the chromic acid was in excess. This preliminary indication of trivalent tin will be further investigated.

Summary

1. When chromic acid is partially reduced by ferrous sulfate, mercurous sulfate, stannous chloride and oxalic acid, pentavalent chromium has been found as an intermediate product.
2. No evidence has been found for tetravalent chromium.
3. When stannous chloride is partially oxidized by chromic acid, evidence for the existence of trivalent tin has been obtained. This will be further investigated.

ST. LOUIS, MO.

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(10) Mitchell, *J. Chem. Soc.*, **125**, 564 (1925).

[CONTRIBUTION FROM THE FERTILIZER INVESTIGATIONS OF THE BUREAU OF CHEMISTRY AND SOILS, AND THE BUREAU OF STANDARDS]

Low Temperature Specific Heats. IV. The Heat Capacities of Potassium Chloride, Potassium Nitrate and Sodium Nitrate[1]

BY J. C. SOUTHARD AND R. A. NELSON

This paper represents part of a program to obtain data on materials involved in the manufacture of fertilizers. A knowledge of the thermal properties of both potassium chloride and nitrate is of importance in connection with the process recently considered by Whittaker, Lundstrom and Merz.[2]

Measurements of the heat capacity of potassium chloride over temperature intervals sufficiently small to make possible the determination of specific heat as a function of temperature were made by Nernst,[3] and by Lindemann and Schwers.[4] Koref[5] and others have also measured a few "mean" specific heats. No published data on the specific heats of potassium and sodium nitrate have been found at low temperatures.

TABLE I

THE MOLAL HEAT CAPACITY OF SODIUM NITRATE FROM 15 TO 285°K., 0°C. = 273.16°K.

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
16.23	0.454	64.40	8.197	136.79	14.99	220.08	18.91
19.78	.827	67.32	8.670	142.24	15.33	225.13	19.13
22.92	1.222	67.67	8.694	147.63	15.72	230.18	19.33
23.29	1.273	71.90	9.251	152.98	15.98	235.21	19.55
26.78	1.785	71.94	9.238	158.30	16.24	240.24	19.77
27.56	1.927	76.22	9.842	163.59	16.52	245.25	20.08
30.03	2.312	80.61	10.40	164.48	16.59	247.21	20.04
31.84	2.626	85.37	11.04	168.85	16.72	250.25	20.18
33.85	2.974	90.20	11.49	169.70	16.74	255.45	20.46
35.63	3.279	91.42	11.56	174.09	16.96	258.16	20.52
38.80	3.847	94.87	11.97	174.90	16.97	260.65	20.64
40.08	4.059	96.60	12.12	180.09	17.21	263.04	20.72
44.35	4.805	99.42	12.37	185.25	17.45	267.91	21.00
45.90	5.075	101.61	12.55	190.39	17.65	272.77	21.15
49.73	5.752	106.51	12.96	204.86	18.26	277.23	21.37
51.57	6.143	111.30	13.33	207.61	18.39	277.62	21.35
54.91	6.688	116.00	13.69	209.95	18.47	282.06	21.58
56.99	6.921	120.62	14.05	214.99	18.73	282.47	21.56
59.64	7.469	125.72	14.36	215.02	18.74	286.86	21.78
62.37	7.888	131.29	14.74	220.06	18.92		

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(1) Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

(2) C. W. Whittaker, F. O. Lundstrom and A. R. Merz, *Ind. Eng. Chem* **23**, 1410 (1931).

(3) Nernst, *Ann. Physik*, [4] **36**, 419 (1911); also Nernst and Lindemann, *Z. Elektrochem.*, **17**, 817 (1911).

(4) Lindemann and Schwers, *Physik. Z.*, **14**, 67 (1913).

(5) Koref, *Ann. Physik*, [4] **36**, 59 (1911).

The material used for these measurements was of C. P. quality, further purified by Dr. C. W. Whittaker by three or four recrystallizations. The salts were dried in a high vacuum with a liquid air trap to collect the water pumped off. Potassium chloride required further treatment as described later.

TABLE II

THE MOLAL HEAT CAPACITY OF POTASSIUM NITRATE FROM 15 TO 295°K.

T, °K.	C_p cal./mole/ deg.	*T*, °K.	C_p cal./mole/ deg.	*T*, °K.	C_p cal./mole/ deg.	*T*, °K.	C_p cal./mole/ deg.
15.96	0.664	93.95	13.95	159.62	17.54	233.04	20.39
19.52	1.159	94.01	13.97	164.93	17.76	238.53	20.51
23.45	1.787	98.68	14.33	170.22	17.99	238.90	20.58
27.28	2.601	98.74	14.32	175.49	18.17	243.75	20.74
27.41	2.593	103.38	14.71	180.76	18.33	244.12	20.73
31.07	3.552	108.23	15.03	186.03	18.54	248.96	20.97
36.78	4.808	113.30	15.31	191.28	18.81	249.33	20.97
41.37	5.928	118.31	15.65	196.12	18.96	254.53	21.13
46.20	6.886	123.26	15.91	196.53	18.93	259.73	21.37
51.57	8.069	128.17	16.16	201.37	19.14	264.93	21.53
56.86	9.159	133.31	16.45	201.79	19.12	270.11	21.84
61.79	10.05	138.69	16.70	206.62	19.32	275.29	21.95
66.43	10.76	143.63	16.92	207.03	19.36	280.46	22.19
71.16	11.42	144.04	16.97	211.87	19.55	285.63	22.41
74.84	11.85	148.98	17.07	212.27	19.55	290.78	22.70
84.24	13.08	149.36	17.18	217.11	19.74	295.92	22.93
89.15	13.55	154.30	17.38	222.34	19.99		
89.20	13.58	154.68	17.33	227.56	20.14		

TABLE III

THE MOLAL HEAT CAPACITY OF POTASSIUM CHLORIDE (FUSED) FROM 15 TO 285°K.

T, °K.	C_p cal./mole/ deg.	*T*, °K.	C_p cal./mole/ deg.	*T*, °K.	C_p cal./mole/ deg.	*T*, °K.	C_p cal./mole/ deg.
16.69	0.427	96.10	9.204	179.76	11.36	229.29	11.85
21.21	.842	101.31	9.438	183.41	11.39	230.28	11.86
25.06	1.302	106.43	9.656	184.85	11.41	235.01	11.86
28.81	1.810	111.48	9.842	185.22	11.45	235.93	11.91
32.41	2.360	116.47	10.03	188.83	11.47	240.70	11.92
36.00	2.917	121.41	10.17	190.32	11.48	241.62	11.95
39.86	3.533	126.32	10.34	194.28	11.51	246.41	11.98
44.25	4.189	131.19	10.46	195.81	11.53	247.32	11.98
49.27	4.926	136.04	10.61	199.74	11.56	252.15	12.00
54.44	5.671	141.17	10.76	201.32	11.59	252.68	12.02
59.61	6.326	146.58	10.85	205.23	11.64	257.80	12.03
64.94	6.893	152.30	10.95	206.85	11.69	257.91	12.06
69.92	7.365	158.02	11.06	210.73	11.69	262.94	12.01
74.62	7.761	163.45	11.14	212.40	11.72	263.70	12.10
79.11	8.158	168.88	11.21	216.26	11.73	268.15	12.05
84.10	8.549	172.60	11.26	217.97	11.75	269.52	12.15
89.28	8.844	174.31	11.28	219.04	11.76	273.34	12.15
90.80	8.904	177.99	11.33	223.61	11.80	278.54	12.20
94.32	9.123	179.39	11.36	224.65	11.81	284.68	12.25

TABLE IV

THE MOLAL HEAT CAPACITY OF POTASSIUM CHLORIDE (HEATED TO 700°) FROM 90 TO 290°K.

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
92.26	9.024	146.29	10.85	187.01	11.48	239.20	11.93
96.84	9.248	151.13	10.93	192.72	11.53	245.11	12.02
101.70	9.459	152.99	10.99	198.44	11.63	251.05	12.06
106.86	9.675	155.97	11.04	204.18	11.63	257.02	12.10
111.94	9.851	158.65	11.05	209.95	11.69	263.03	12.14
116.96	10.05	164.31	11.19	215.74	11.71	269.06	12.17
121.93	10.19	169.88	11.24	221.59	11.76	275.12	12.23
126.86	10.36	175.64	11.36	227.42	11.83	281.20	12.31
136.58	10.62	181.29	11.40	233.30	11.85	287.30	12.34
141.44	10.73						

The measurements were made with the calorimeter described previously[6] and the data are shown in Tables I–IV and Fig. 1. The results are expressed in calories (one calorie = 4.1833 int. joules = 4.185 absolute joules). The errors were discussed in connection with the description of the apparatus. All weights are corrected to vacuum.

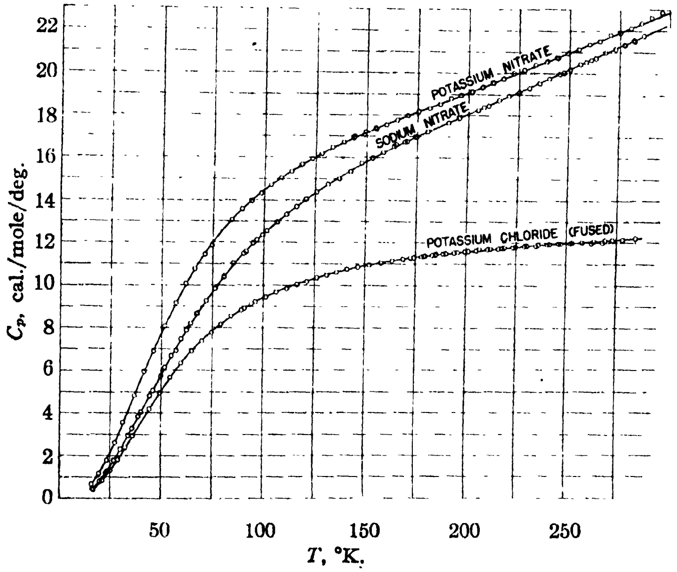

Fig. 1.—Heat capacities of potassium chloride, potassium nitrate and sodium nitrate as a function of temperature in the range 15 to 290°K.

The entropy from 15 to 298.16°K. was determined by plotting the experimentally found molal heat capacity against log T and integrating graphically. To find the entropy from 0 to 15°K., a characteristic temperature,

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[6] Southard and Brickwedde, THIS JOURNAL, 55, 4378 (1933).

Θ_D, was calculated for each experimental point up to 40°K., assuming three degrees of freedom for each ion (a total of six for the molecule). The Θ_D found in this manner did not vary appreciably from 15 to 40°K. and was used, with the tables of Simon,[7] to find the entropy at 15°K.

The results of the entropy calculations were as follows:

	KCl (fused) cal./mole/deg.	KNO_3 cal./mole/deg.	$NaNO_3$ cal./mole/deg.
$(S_{298.16^\circ}-S_{15^\circ})$ graph.	19.65 ± 0.04	31.58 ± 0.06	27.75 ± 0.06
$(S_{15^\circ}-S_{0^\circ})$ calcd.	0.10 ± .02 ($\Theta_D = 218$)	0.19 ± .04 ($\Theta_D = 178$)	0.12 ± .02 ($\Theta_D = 206$)
$S_{298.16}-S_0$ total	19.75 ± .06	31.77 ± .10	27.87 ± .08

Two different samples of potassium chloride were dried as described above, one for two and one for five days. Both samples showed a region of about 10° in which the heat capacity was abnormally high, the maximum of the "hump" occurring at about −10°. Since the presence of occluded water was suspected, two further samples were prepared, one by heating to 700° and the other by fusion with subsequent grinding. All heating was done in platinum vessels. Measurements showed the heat capacities of these two latter samples to be free from abnormalities and coincident from the lowest temperatures up to about −13°. The results at low temperatures were in good agreement with the results on the unheated salt. Above this temperature the specific heat of the heated but unfused salt appeared to be about 0.5% higher than that of the fused. The entropy difference at 298.16°K. between unfused and fused chloride was less than 0.02 cal./mole/degree.

The free energy of formation of these salts may now be calculated by the third law of thermodynamics using the heats of formation given in the "I. C. T.," Vol. V, the entropies of sodium and potassium as given by Kelley,[8] and the entropies of oxygen, chlorine, and nitrogen as given by Giauque and co-workers.[9] The results are summarized below.

Reaction ($T = 298.16$°K.)	ΔH° cal./mole	ΔS° cal./mole/deg.	ΔF° cal./mole
$Na + 1/2N_2 + 3/2O_2 = NaNO_3$	−112,410	−80.77	−88,300
$K + 1/2N_2 + 3/2O_2 = KNO_3$	−118,780	−79.87	−95,000
$K + 1/2Cl_2 = KCl$	−104,300	−22.11	−97,700

The authors are indebted to F. G. Brickwedde for his help and encouragement in the work. The assistance of R. T. Milner in the preparation of materials and in the measurements is gratefully acknowledged.

Summary

1. The molal heat capacities of potassium chloride, potassium nitrate and sodium nitrate have been determined in the range from 15 to 290°K.

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(7) "Handbuch d. Physik," Vol. X, p. 370.

(8) Kelley, Bureau of Mines Bull. 350 (1932).

(9) Giauque and Johnston, THIS JOURNAL, 51, 2300 (1929); Giauque and Overstreet, *ibid.*, 54, 1731 (1932); Clayton and Giauque, *ibid.*, 54, 2610 (1932).

2. The molal entropies of these compounds at 298.16°K. are found to be 19.75 ± 0.06, 31.77 ± 0.10 and 27.87 ± 0.08 cal./mole/deg., respectively.
3. The free energies of formation of these salts from the elements have been calculated.

WASHINGTON, D. C.

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Magnetic Susceptibilities of Some Europium and Gadolinium Compounds

BY P. W. SELWOOD

The objects of this work were: (1) to provide an experimental check on the theoretical magnetic behavior of the trivalent europium ion at low temperatures,[1] (2) to determine to what extent the Sommerfeld–Kossel rule is followed by the ions Eu^{++} and Gd^{+++}, and if possible, to evaluate the spectral term of Eu^{++} from the temperature coefficient of magnetic susceptibility, and (3) by means of magnetic measurements on different gadolinium compounds to examine the influence of the Heisenberg exchange interaction with more precision than was possible in the writer's previous work[2] on neodymium, which, not being in an S state, is subject to the effect of the crystalline field on the orbital component of the magnetic moment.

Magnetic measurements on europium in the oxide and anhydrous sulfate from room temperature to 600° have been made by Cabrera and Duperier,[3] while the oxide has been examined from 183 to 673° by Sucksmith.[4] The values obtained are in fair agreement with the theoretical. However, as measurements on "magnetically dilute" substances are much to be preferred, data are given here on the octahydrated sulfate.

The only measurement made on the recently prepared compound europous sulfate is that of Hughes and Pearce,[5] who find a value some 15% lower than for gadolinium. Their work is open to the criticisms that the temperature is not stated explicitly, it is not stated what diamagnetic corrections, if any, have been made, and, finally, water, which they used for calibration, is very unsatisfactory for the measurement of a susceptibility 140 times as large.

The gadolinium compounds examined were the oxide, anhydrous chloride, and octahydrated sulfate. The first has been studied by Williams[6] over a large temperature range, and also by Cabrera and Duperier,[3] while the last was the subject of the celebrated measurement of Woltjer and Onnes[7] from 1.3 to 294°K. As the author's purpose here was evaluation of the molecular field constant Δ in the familiar Weiss law $\chi = C/(T + \Delta)$, it seemed advisable to remeasure these susceptibilities. As previously pointed out, for any worth-while conclusions to be drawn it seems essential that measurements should be made on the same original rare earth material, where different compounds are being investigated.

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(1) Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, 1932.
(2) Selwood, THIS JOURNAL, 55, 3161 (1933).
(3) Cabrera and Duperier, *Compt. rend.*, 188, 1640 (1929).
(4) Sucksmith, *Phil. Mag.*, [VII] 14, 1115 (1932).
(5) Hughes and Pearce, THIS JOURNAL, 55, 3277 (1933).
(6) Williams, *Phys. Rev.*, 14, 348 (1920).

Experimental Part

Apparatus.—The apparatus used was the Gouy magnetic balance previously described[2] with a few minor improvements giving a slightly greater field strength and better temperature control. The apparatus was calibrated with a solution of nickel chloride prepared as before, and also with a pure sample of hydrated ferrous ammonium sulfate (Mohr's salt) for which from Jackson's[8] measurements $C = 9500 \times 10^{-6}$, and $\Delta = 1°$ in the relation $\chi = C/T + \Delta$ where χ is the specific susceptibility and T the absolute temperature. The two calibrations agreed well.

Preparation of Materials.—The europium used in this work was of "atomic weight" purity[9] prepared in the Chemical Laboratory of the University of Illinois. The gadolinium[10] had been prepared at the University of Illinois by Dr. L. L. Quill and the writer during the years 1927–1930. Examination by means of the arc spectrum showed that it was free from europium and contained less than 0.2% of terbium, which would at most raise the magnetic susceptibility by 0.3%. This is slightly less than the maximum probable error in the measurements themselves. In view of the fractionation method used, the gadolinium must have been free from all other elements.

Europium oxide was prepared as usual by ignition of the oxalate. The octahydrated sulfate was prepared by a method analogous to that used for the neodymium salt in the writer's previous work.

Europous sulfate ($EuSO_4$) was prepared by electrolytic reduction in the presence of sulfuric acid according to Yntema's[11] method. Reduction at an amalgamated lead cathode in place of mercury proved unsatisfactory. The compound was washed with alcohol and ether and was dried at 65°. It showed no sign of oxidation after standing in a vacuum desiccator for several days. It was analyzed by oxidation with a little concentrated nitric acid followed by precipitation as oxalate and ignition to oxide. The mean of two closely agreeing analyses gave a weight of Eu_2O_3 less than 0.5% less than the theoretical.

Anhydrous gadolinium chloride was prepared by slow dehydration of the hydrated salt in a stream of dry hydrogen chloride gas.[12] The oxide and sulfate octahydrate were prepared in the usual manner.

In general the writer adhered to the precautions previously described in detail.

Results

In the tables χ_s is the specific (gram) susceptibility, χ_M the molar susceptibility, and χ_{Eu} or χ_{Gd} the susceptibility per gram ion of the trivalent ions corrected for the diamagnetism of anion, crystal water, and cation, the last being estimated[2] as -30×10^{-6}. Δ is given in °C.

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[7] Woltjer and Onnes, *Proc. Acad. Sci. Amsterdam*, **26**, 626 (1923).

[8] Jackson, *Trans. Roy. Soc.* (London), **A224**, 1 (1923).

[9] Preparation and criteria of purity will be described in a forthcoming paper in THIS JOURNAL by Quill and Selwood.

[10] The writer is indebted to Professor B. Smith Hopkins of the University of Illinois for the loan of both europium and gadolinium used in this work.

[11] Yntema, THIS JOURNAL, **52**, 2782 (1930).

[12] See for instance Little, "Text-Book of Inorganic Chemistry," Vol. IV (Friend). Griffin, London 1917.

TABLE I

$Eu_2(SO_4)_3 8H_2O$, mol. wt. 728.2, molar diamagnetic correction -335×10^{-6}

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Eu} \times 10^6$
343	12.3	8920	4630
293	13.1	9540	4940
223	14.6	10630	5480
153	16.2	11780	6060
83	17.0	12400	6370

Eu_2O_3, mol. wt. 352, molar diamagnetic correction -99×10^{-6}

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Eu} \times 10^6$
373	27.8	9800	4950
293	31.3	11020	5560
223	35.7	12560	6330
153	42.2	14860	7480
83	47.8	16830	8470

The experimental and theoretical effective Bohr magneton numbers are given in Table V.

TABLE II

$EuSO_4$, mol. wt. 248.1, molar diamagnetic correction -67×10^{-6}, $\Delta = 4°$

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Eu} \times 10^6$	$1/\chi_{Eu} \times 10^{-4}$	$\chi_{Eu}(T + \Delta)$
343	88.5	21950	22020	0.4540	7.64
293	103.8	25730	25800	.3880	7.66
223	135.4	33580	33650	.2970	7.64
153	195.3	48430	48500	.2060	7.62
83	353.3	87630	87700	.1140	7.63

TABLE III

Gd_2O_3, mol. wt. 362.5, molar diamagnetic correction -99×10^{-6}, $\Delta = 18°$

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Gd} 10^6$	$1/\chi_{Gd} \times 10^{-4}$	$\chi_{Gd}(T + \Delta)$
373	107.4	38900	19500	0.514	7.64
293	135.0	48900	24500	.408	7.62
223	173.5	62900	31500	.317	7.62
153	244.7	88700	44400	.225	7.63
83	414.5	150300	75200	.133	7.60
$GdCl_3$, mol. wt. 263.6, molar diamagnetic correction -90×10^{-6}, $\Delta = 14°$					
373	74.7	19700	19800	0.505	7.66
293	94.8	25000	25100	.399	7.70
223	123.0	32400	32500	.308	7.70
153	174.5	46000	46100	.217	7.70
83	300.5	79200	79300	.126	7.69
$Gd_2(SO_4)_3 \cdot 8H_2O$, mol. wt. 746.8, molar diamagnetic correction -335×10^{-6}, $\Delta = 2°$					
343	62.7	46800	23500	0.425	8.11
293	73.4	54800	27500	.364	8.11
223	95.9	71600	35900	.278	8.09
153	139.3	104000	52100	.192	8.08
83	254.8	190200	95200	.105	8.10

It is of interest to compare the above results with earlier work. Values available up to 1926 are summarized by Zernike and James.[13] Work since that time has been published by Cabrera and Duperier,[3] by Sucksmith,[4]

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(13) Zernike and James, THIS JOURNAL, 48, 2827 (1926).

and by Hughes and Pearce.[5] For purposes of comparison all data are converted (interpolated where necessary) to specific susceptibility at 20° with no corrections.

TABLE IV

COMPARISON OF EXPERIMENTAL RESULTS AT 20°

	$\chi_s \times 10^6$					
	Eu_2O_3	$Eu_2(SO_4)_3 \cdot 8H_2O$	$EuSO_4$	Gd_2O_3	$GdCl_3$	$Gd_2(SO_4)_3 \cdot 8H_2O$
Urbain	28.9	..	..	135.6	..	..
S. Meyer	..	15.4	..	...	..	75.1
Cabrera	..	15.4	..	...	..	74.3
Woltjer and Onnes	..	..	..	...	..	68.6 72.2
Zernike and James	..	..	..	...	..	68.8
Williams	..	..	..	129.8	..	..
Cabrera and Duperier	26.6	..	..	139.3	..	70.8
Sucksmith	26.1	..	..	...	..	..
Hughes and Pearce	..	15.0	83.5	...	..	68.9
Selwood	31.3	13.1	103.8	135.0	94.8	73.4

Some comment on these data seems to be called for. The general agreement is far from good, although some discrepancies may be due to misunderstandings on the writer's part as to the diamagnetic corrections and temperatures applying to some of the published data. The most startling discrepancy is in the case of europous sulfate. It is difficult to see how the writer's value could be noticeably too high, and this value is, as predicted by the Sommerfeld–Kossel rule, close to that for gadolinium, while the value of Hughes and Pearce is about 20% lower. In connection with Sucksmith's low value for europium oxide, it may be pointed out that his results for neodymium and ytterbium are also considerably lower than those of other investigators, that for the ytterbium even being about 13% lower than the surprisingly low value reported by Hughes and Pearce.

With regard to the values of Δ for the gadolinium salts, Woltjer and Onnes found for the sulfate octahydrate $\Delta = 0$. This is within the writer's probable error in his value $\Delta = 2$. Williams found for the oxide $\Delta = 9$, while Cabrera and Duperier found $\Delta = 13.3$.

Discussion of Results

The early calculations by Hund[14] led to values for the magnetic moments of the rare earths in good agreement with observed values except for samarium and europium. Various speculations were made as to why the disagreement should occur, until it was shown by Van Vleck and Miss Frank[15] that in the cases of these two elements (and illinium) the multiplet intervals are not infinitely large compared to kT, so that the approximations in Hund's calculation are not sufficient. The predictions for samarium have already been reasonably well verified.[16] Van Vleck also

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(14) Hund, *Z. Physik*, **33**, 855 (1925).

(15) Van Vleck and Frank, *Phys. Rev*, **34**, 1494, 1625 (1929).

(16) Freed, THIS JOURNAL, **52**, 2702 (1930).

showed that a fairly large part of the paramagnetism of europium should be independent of temperature. It is the writer's purpose merely to set down Van Vleck's theoretical values and to compare them with the observed data. Only the sulfate octahydrate data are used for reasons mentioned above.

For this comparison all data are converted to "effective Bohr Magneton" numbers. These are given by $\mu_{\text{eff.}} = \sqrt{3\chi_{\text{Eu}}\,kT/L\,\beta^2}$, where k is the Boltzmann number, L Avogadro's number and β the Bohr magneton 0.9174×10^{-20} e. m. u. In the theoretical computation there exists some uncertainty as to whether the screening constant for europium should be $\sigma = 33$ or 34. Therefore two theoretical values for $\mu_{\text{eff.}}$ are given and it was at first hoped that this work would provide a means of deciding which screening constant is most probable.

There is, however, another consideration in the examination of the experimental data. For ions obeying the Weiss law $\chi = C/T + \Delta)$, Δ frequently remains fairly large (Δ for Nd $= 45°$) even at the highest magnetic dilution provided the ion is not in an S state. Part at least of Δ in this case is due to the orienting influence of the crystalline field, or field of oriented solvent molecules. Although europium does not obey the Weiss law, there seems to be no reason why the crystalline field should not act in the same manner here as for the other members of the rare earth group. The writer has therefore included in Table V values of $\mu_{\text{eff.}}$ calculated from $\mu_{\text{eff.}} = \sqrt{3\chi_{\text{Eu}}\,k(T + \Delta)/L\,\beta^2}$ where $\Delta = 10$, and 22. In order that the significance of these figures may more readily be grasped they are shown graphically in Fig. 1.

TABLE V

EFFECTIVE BOHR MAGNETON NUMBERS FROM $Eu_2(SO_4)_3 8H_2O$

	$\mu_{\text{eff.}}$ theoretical		$\mu_{\text{eff.}}$ experimental		
Temp., °K.	$\sigma = 33$	$\sigma = 34$	$\Delta = 0$	$\Delta = 10$	$\Delta = 22$
343	3.55	3.64	3.58	3.63	3.68
293	3.40	3.51	3.41	3.47	3.53
223	3.19	3.29	3.14	3.21	3.28
153	2.82	2.94	2.73	2.82	2.92
83	2.18	2.32	2.06	2.18	2.32

There is, of course, little justification for inserting these arbitrary figures 10 and 22, except that they are not unreasonable values compared with those found for praseodymium and neodymium. With $\Delta = 10$ the experimental values are in fair agreement with the theoretical when $\sigma = 33$. With $\Delta = 22$ the agreement is extremely good for $\sigma = 34$. It is to be hoped that a calculation such as that of Penney and Schlapp[17] for the crystalline fields of neodymium and praseodymium sulfate octahydrates may be made for europium to show which Δ, if either, is the more probable. This should settle the screening constant question once and for all.

(17) Penney and Schlapp, *Phys. Rev.*, **41**, 194 (1932).

The susceptibility of the Eu^{++} ion is in very gratifying agreement with that of Gd^{+++}. The compound $EuSO_4$ is scarcely as magnetically dilute as might be desired, but the chemistry of divalent europium is so little known that it scarcely seemed worth while to attempt the preparation of other compounds. With such a compound as $EuSO_4$ it might be expected that the exchange interaction would be appreciable, and the value $\Delta = 4$ is a little lower than might have been anticipated. It indicates, however, that the correspondence $\chi_{Eu^{++}} = \chi_{Gd^{+++}}$ is not accidental, if such a possibility can be considered. No ion other than one in an S state could have such a low value for Δ. The electronic configuration of the europous ion must, therefore, be identical with that of trivalent gadolinium.[18]

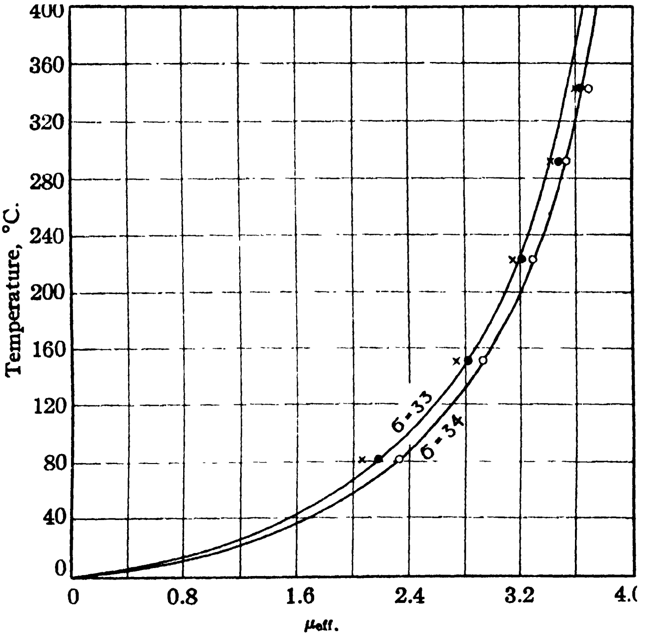

Fig. 1.—Effective Bohr magneton numbers of europium. Solid lines are theoretical for screening constants 33 and 34. Experimental points X are for $\Delta = 0$; ● for $\Delta = 10$, and O for $\Delta = 22$ in $\mu_{eff.} = \sqrt{3\chi_{Eu}k(T + \Delta)/L\beta^2}$.

As in the case of neodymium, the value of Δ in the gadolinium compounds is proportional to the magnetic concentration, with the difference that the effect in gadolinium is not complicated by orbital dissymmetry. The values for Δ in Nd_2O_3 = 59°, NdF_3 = 54°, $Nd_2(SO_4)_3 8H_2O$ = 45°, and Gd_2O_3 = 18, $GdCl_3$ = 14, $Gd_2(SO_4)_3 \cdot 8H_2O$ = 2 (or 0) show that the exchange forces are roughly the same in both cases. As Δ, at least in ferro-magnetic substances, is readily related to the Heisenberg exchange integral, it may be possible to evaluate the variation of the integral with interionic distance when crystal structure data on the various gadolinium compounds are available. As in the case of neodymium the fairly large variation in Curie constant from one compound to another remains unexplained.

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[18] As suggested by Hughes and Pearce, this, of course implies that the remaining outer electron, probably one of the 5d electrons, slips back into the 4f shell in Eu^{++}. Its ready removal again is attested by the ease of the oxidation $Eu^{++} \longrightarrow Eu^{+++}$.

Summary

The magnetic susceptibilities of Eu_2O_3, $Eu_2(SO_4)_3 \cdot 8H_2O$, $EuSO_4$, Gd_2O_3, $GdCl_3$, and $Gd_2(SO_4)_3 \cdot 8H_2O$ have been measured from −190 to 70 or 100°. The effective Bohr magneton numbers for europium are in good agreement with quantum mechanical predictions. The susceptibility and electronic configurations of Eu^{++} are the same as those of Gd^{+++}. The Heisenberg exchange interaction forces for the gadolinium compounds are shown to be proportional to the magnetic concentration as in the case of neodymium.

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The Heat Capacity and Entropy of Nitrogen. Heat of Vaporization. Vapor Pressures of Solid and Liquid. The Reaction $^1/_2\ N_2 + {}^1/_2\ O_2 = NO$ from Spectroscopic Data

BY W. F. GIAUQUE AND J. O. CLAYTON[1]

Besides being one of the more important elements nitrogen is interesting as a light molecule possessing two non-combining forms comprised of the alternate rotation states. Thus one of the principal reasons for the present investigation is to decide whether the lack of equilibrium between the two forms persists into the solid state in some manner similar to that existing in solid hydrogen. It will be shown later that like iodine[1a] and unlike hydrogen, the type consisting of the odd rotational levels of the normal electronic state loses, in solid nitrogen, the rotational *a priori* weight of three associated with the lowest state in the gas. The three states are replaced by one and that, presumably, is a vibrational rather than a rotational state. This corresponds to the expectation of Pauling.[2]

The present work on nitrogen also includes a calculation of its free energy from band spectra.

Preparation of Nitrogen.—The nitrogen was prepared by passing gaseous ammonia into bromine water: $8NH_3 + 3Br_2 = 6NH_4Br + N_2$. About twenty-five or thirty moles of bromine was used for each preparation. In the first experiment ammonium bromide was used to increase the solubility at the start. However, the ammonium

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(1) Shell Research Fellow, Academic year 1929–1930.

(1a) Giauque, THIS JOURNAL, 53, 507 (1931).

(2) Pauling, *Phys. Rev.*, 36, 430 (1930).

bromide formed during reaction precipitated and increased the difficulty of dissolving the bromine from the layer on the bottom. Later a water solution of bromine was used at the start to minimize this difficulty. The reaction vessel was cooled with ice to prevent the heat of reaction from raising the vapor pressure of the bromine to an undesirable extent. The gas evolved usually contained excess bromine. Most of this was returned to the reaction flask by means of an ice jacketed condenser. The gas was passed through a train containing solid potassium hydroxide (sticks), anhydrous copper sulfate, a 50% solution of potassium hydroxide, concentrated sulfuric acid, solid potassium hydroxide (sticks) and phosphorus pentoxide. The anhydrous copper sulfate was used to absorb ammonia and indicate when ammonia was coming through the system due to depletion of bromine in the water layer.

All solutions were boiled under vacuum and the train was evacuated. This method precluded the presence of oxygen, which would have been difficult to remove. The nitrogen was distilled three times, a small first fraction and the last quarter being discarded each time. The very small first fraction was all that was considered necessary to discard as there were no possible impurities more volatile than nitrogen.

Heat Capacity Measurements and Data.—The apparatus, known as Gold Calorimeter II, and the method have been described previously.[3] Three preparations were used for the measurements. The amounts were measured volumetrically as previously described.[3b] In this connection the following constants were used in the equation.

Number of moles $= V \times P \times (D/M) \times 1/(1 + KT)\,[1 + \alpha(1 - P)]$
Gas density at 0° and 760 mm. $D = 1.25057$ g./l.[4,5,6a,b,7]
Molecular weight $M = 28.016$
Coefficient of thermal expansion $K = 0.0036777$[8,9a,b]
Coefficient of deviation from Boyle's law $\alpha = -0.00047$[10]
Gravitational acceleration (for Berkeley)[11] $= 979.973$ cm./sec.^{2}

The latter value was used to convert pressure measurements to the international scale. In correcting for the heat effect due to evaporation into the small gas volume above the liquid or solid nitrogen during a temperature rise, the density of the condensed material was necessary.

For liquid nitrogen Baly and Donnan[12] give $d = 1.1604 - 0.00455\,T$.

For solid nitrogen Dewar[13] gives 1.0265 at 20.6°K. and 0.8792 g./cc. at 63°K.

The volume of the gold calorimeter was 112.8 cc. at 20°.

The calorimetric data are given in Table I and are shown graphically in

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(3) (a) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928); (b) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

(4) Gray, *J. Chem. Soc.*, **87**, 1601 (1905).

(5) Moles, *J. chim. phys.*, **19**, 283 (1921).

(6a) Moles and Clavera, *Añales soc. españ. fís. quim.*, **20**, 550 (1922).

(6b) Moles and Clavera, *J. chim. phys.*, **21**, 10 (1924).

(7) Baxter and Starkweather, *Proc. Am. Acad. Arts Sci.*, **12**, 703 (1926).

(8) Chappuis, *Trav. et Mem. bur. intern. des poids et measures*, 13 (1907).

(9a) Holborn and Otto, *Z. Physik*, **23**, 77 (1924).

(9b) Holborn and Otto, *ibid.*, **30**, 320 (1924).

(10) "International Critical Tables."

(11) Sternewarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Berlin, 1923.

(12) Baly and Donnan, *J. Chem. Soc.*, **81**, 907 (1902).

(13) Dewar, *Proc. Roy. Soc.* (London), **A73**, 251 (1904).

TABLE I

HEAT CAPACITY OF NITROGEN

Molecular weight, 28.016. Series I, 2.7338 moles; Series II, 2.5855 moles; Series III, 2.5558 moles.

T, °K. mean	ΔT	C_p Cal. per degree per mole	Series
15.82	1.520	3.124	III
17.66	1.632	3.840	III
19.51	1.722	4.577	III
21.94	1.943	5.447	III
24.49	2.716	6.331	II
24.85	3.597	6.380	III
27.14	2.330	7.170	II
28.32	3.139	7.540	III
29.89	2.722	8.137	II
31.29	2.656	8.643	III
32.84	1.929	9.397	III
34.42	0.185	10.28	III
34.68	.487	10.49	III
35.05	.315	10.84	III
35.33	.389	10.67	III
35.61	Transition		
39.13	3.821	8.948	II
43.27	3.797	9.325	II
48.07	3.703	9.752	II
51.88	3.681	10.09	II
53.55	4.345	10.26	III
55.88	3.967	10.44	II
57.99	4.400	10.65	III
61.40	2.341	11.09	I
61.41	2.229	11.07	III
63.14	Melting Point		
65.02	2.184	13.33	I
68.41	4.455	13.45	I
70.28	4.149	13.45	I
72.69	3.880	13.56	I
74.57	4.228	13.59	I
76.58	3.715	13.68	I
77.74	1.858	13.64	I

Fig. 1. In calculating the energy one international joule was taken as 1.0004 absolute joules and 1 calorie (15°) was taken as 4.185 absolute joules.

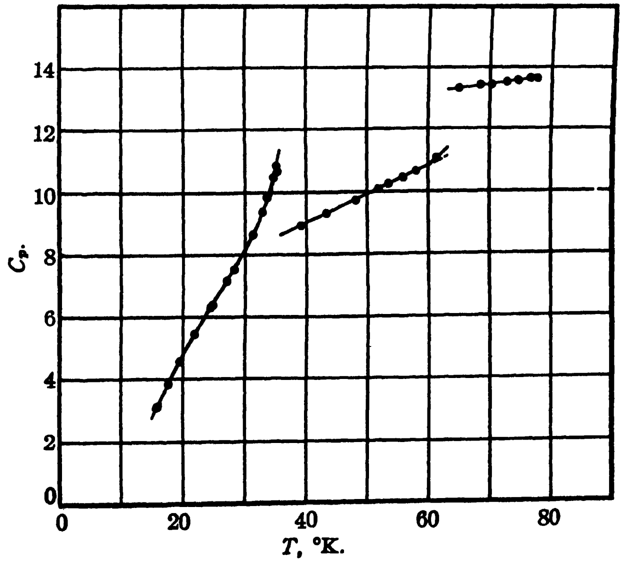

Fig. 1.—Heat capacity in calories per degree per mole of nitrogen.

Assuming that the slight rise in heat capacity below the melting point is due to premelting caused by impurity, it is computed that such impurity is not over three thousandths of one mole per cent. However, it is possible that even this small rise is characteristic of the pure substance.

The heat capacity of nitrogen has been measured by Eucken,[14] by Clusius[15] and by Wiebe and Brevoort.[16] The results of Clusius agree fairly well with those of the present investigation; the maximum deviation in the solid range is 4%. In the liquid range his measurements are consistently higher by 1.5%. The average deviation of Clusius' results from the above work is about 2%; the average algebraic deviation is 0.8%. The earlier work of Eucken agrees almost as well as that of Clusius. The results on the liquid are consistently 1.5% lower than the present work. The work of Wiebe and Brevoort covered only the liquid range at high pressures; the results of their work and the present work are in very satisfactory agreement in the neighborhood of the boiling point.

Transition and Melting Point Temperatures.—The transition and melting point temperatures were observed with various percentages transformed. All of the measurements were obtained on the material used in Series II. The transition temperature was observed over a period of fifteen hours. The melting point was observed on four occasions designated a, b, c and d, over periods of nineteen, thirty-five, eight and twelve hours, respectively. The data are given in Table II.

TABLE II

TRANSITION AND MELTING POINT TEMPERATURES OF NITROGEN

Transition temperature			Melting point		
Per cent. transformed	T, °K.	Series	Per cent. transformed	T, °K.	Series
25	35.59	II	50	63.12	IIb
25	35.59	II	50	63.12	IIb
70	35.63	II	60	63.12	IIb
70	35.64	II	75	63.10	IIb
Average	35.61 ± 0.05		10	63.14	IIc
			10	63.14	IIc
	Melting point		20	63.14	IIc
5	63.13	IIa	20	63.14	IIc
5	63.13	IIa	30	63.14	IIc
45	63.13	IIa	40	63.14	IIc
5	63.12	IIb	50	63.13	IIc
5	63.12	IIb	70	63.13	IId
			Average (c, d)	63.14 ± 0.05	

The conditions for measuring the melting point were not as satisfactory in Series a and b as in c and d, so that only the latter two were used in computing the final value 63.14. The experiments of series c were used for the triple point pressure measurements given in Table V. In Table III the data of previous observers have been collected.

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(14) Eucken, *Ber. deut. physik. Ges.*, **18**, 4 (1916).

(15) Clusius, *Z. physik. Chem.*, **B3**, 41 (1929).

(16) Wiebe and Brevoort, THIS JOURNAL, **52**, 622 (1930).

TABLE III

SUMMARY OF AVAILABLE TRANSITION AND MELTING POINT TEMPERATURE DATA FOR NITROGEN

T, °K.		T, °K.	
	Transition temperature	62.6	(1904) Dewar[18]
35.5	(1916) Eucken[14]	62	(1906) Erdmann[20]
35.4	(1919) Clusius[15]	63.17	(1913) Von Siemens[21]
35.61	This research	63.24	(1915) Crommelin[22]
		63.1	(1916) Eucken[14]
	Melting point	63.12	(1927) Henning[23]
70–74	(1886) von Wroblewsky[17]	63.08	(1929) Clusius[15]
59	(1887) Olszewsky[18]	63.14	(1931) Verschoyle[24]
62.58	(1902) Fischer and Alt[19]	63.14	This research

Heats of Transition and Fusion.—The heats of transition and fusion were measured in the usual manner, starting the energy input a little below the transition or melting temperature and ending a little above. A correction for $\int C_p\, dT$ was made. The results are given in Table IV, which also includes the values given by other observers.

TABLE IV

HEATS OF TRANSITION AND FUSION OF NITROGEN

Molecular weight 28.016

ΔH Transition, calories per mole		ΔH Fusion	
54.79	Series II	172.7	Series II
54.63	Series III	172 4	Series III
54.71 ± 0.1	Average this research	171.9	Series I
53.8	(1916) Eucken[14]	172.3 ± 0.5	Average this research
51.4	(1929) Clusius[15]	168 7	(1916) Eucken[14]
		170.95	(1929) Clusius[15]

Vapor Pressures of Solid and Liquid Nitrogen.—Vapor pressures were measured on the same material used in the calorimetric measurements of Series II. The apparatus and method were approximately the same as previously described by Giauque, Johnston and Kelley.[25] A large diameter manometer was compared with a standard meter by means of a Gaertner cathetometer with an accuracy of 0.05 mm. of mercury. Correction was made for meniscus height.

The results have been represented by equations 1 and 2.

Solid nitrogen 54.78 to 63.14°K.

$$\log P \text{ (cm.)} = (-381.6/T) + 7.41105 - 0.0062372\,T \qquad (1)$$

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(17) Von Wroblewsky, *Compt. rend.*, **102**, 1010 (1886).

(18) Olszewsky, *Wied. Ann. Physik*, **31**, 66 (1887).

(19) Fischer and Alt, *ibid.*, [4] **9**, 1149 (1903).

(20) Erdmann, *Ber.*, **39**, 1207 (1906).

(21) Von Siemens, *Ann. Physik*, [4] **42**, 871 (1913).

(22) Crommelin, *Proc. Roy. Acad. Amsterdam*, **17**, 959 (1915).

(23) Henning, *Z. Physik*, **40**, 775 (1927).

(24) Verschoyle, *Proc. Roy. Soc.* (London), **A230**, 189 (1931).

(25) Giauque, Johnston and Kelley, THIS JOURNAL, **49**, 2367 (1927).

Liquid nitrogen 63.14 to 78.01°K.

$$\log P \text{ (cm.)} = (-339.8/T) + 6.71057 - 0.0056286\, T \qquad (2)$$

The observed and calculated values are given in Table V. The values are given to 0.001° because of the high relative consistency.

TABLE V

VAPOR PRESSURE OF NITROGEN

T, °K. observed	P int. cm. observed	ΔP obs. − calcd.	ΔT obs. − calcd.	Remarks
54.783	1.273	0.003	−0.009	Solid
55.875	1.710	.000	.000	Solid
56.930	2.244	− .010	.017	Solid
57.850	2.840	− .004	.006	Solid
58.741	3.526	− .009	.011	Solid
59.550	4.285	.004	− .004	Solid
60.670	5.526	− .006	.005	Solid
61.700	6.958	.017	− .011	Solid
63.136	9.396			Melting point
	9.400			Melting point
	9.401			Melting point
	9.405			Melting point
	9.397			Melting point
	9.406			Melting point
	9.401			Melting point
Average	9.401 ± 0.005	0.000	0.000	Melting point
64.555	12.105	− .015	.007	Liquid
65.968	15.446	.019	− .007	Liquid
67.367	19.391	.010	− .003	Liquid
68.799	24.255	.027	− .007	Liquid
70.356	30.565	.027	− .006	Liquid
71.947	38.244	− .011	.002	Liquid
73.422	46.673	− .022	.004	Liquid
75.035	57.474	− .028	.004	Liquid
76.528	69.125	+ .002	− .000	Liquid
78.008	82.323	− .002	.000	Liquid

The vapor pressures of the solid have been measured by Olszewsky[26] (at the melting point only), and by von Siemens.[21] The results of von Siemens agree quite well with this work, the greatest deviation being about 0.1°K. Verschoyle[24] has recently measured the triple point pressure. He obtained 9.360 cm. as compared with our value 9.401 cm. Holst's[27] recalculation of von Siemens' results leads to 9.35 cm.

The vapor pressure of liquid nitrogen has been measured by von Wroblewsky,[17] Olszewsky,[26] Baly,[28] Fischer and Alt,[19] Holst and Hamburger,[29] Henning and Heuse,[30] von Siemens[21] and by Cath.[31] Aside

(26) Olszewsky, *Compt. rend.*, **99**, 133 (1884).

(27) Holst, *Comm. Phys. Lab. Leiden* No. 148a (1915).

(28) Baly, *Phil. Mag.*, **49**, 517 (1900).

(29) Holst and Hamburger, *Z. physik. Chem.*, **91**, 513 (1916).

(30) Henning and Heuse, *Z. Physik*, **23**, 105 (1924).

(31) Cath, *Comm. Phys. Lab. Leiden*, No. 152d (1918).

from the pioneer work of Olszewsky and von Wroblewsky, most of these data agree fairly well with the present work. The nitrogen used by Fischer and Alt was impure, melting over a pressure range of from 8.64 to 9.40 cm. The following table gives the approximate average deviations of the above observers from the present work.

Baly	+0.2°	Von Siemens (converted to Leiden temp. scale)	+ 0.05°
Holst and Hamburger	− .07°	Cath	− .03°
Henning and Heuse	− .07°		
Von Siemens	− .03°		

The Boiling Point of Nitrogen.—From Equation 1 the boiling point was found to be 77.32°K. The values of other observers are given in Table VI.

TABLE VI

BOILING POINT OF NITROGEN

T, °K.	Observer	*T*, °K.	Observer
78.6	(1884) Olszewsky[26]	77.32	(1922) Kamerlingh Onnes[33]
80	(1886) von Wroblewsky[17]	77.35	(1924) Henning and Heuse[30]
77.54	(1900) Baly[28]	77.32	(1924) Mathias and Crommelin[34]
77.46	(1902) Fischer and Alt[19]	77.30	(1927) Dodge and Davis[35]
77.75	(1906) Stock and Nielson[32]	77.39	(1927) Henning[23]
77.30	(1918) Cath[31]	77.32	This research

Heat of Vaporization of Nitrogen.—The heat of vaporization was measured directly. The method has been described previously.[3a,b] The

TABLE VII

HEAT OF VAPORIZATION OF NITROGEN

Molecular weight 28.016

ΔH at 760 mm. cal. per mole	Moles N_2 evaporated	Time in minutes	Remarks
1332.4	0.21146	32	Series III
1331.8	.20607	31	Series III
1333.8	.18755	31	Series I
1333.7	.19166	32	Series I
1332.9 ± 1.0	Average this research		
1325.6	Vapor pressure data, using Berthelot's equation to correct for gas imperfection.		
1396	(1903) Shearer[36]		
1411	(1906) Dewar[37]		
1335	(1906) Alt[38]		
1363	(1916) Eucken[14]		
1402	(1922) Hammick[39]		
1337	(1925) Dana[40]		

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(32) Stock and Nielson, *Ber.*, **39**, 2066 (1906).

(33) Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, No. 156a (1922).

(34) Mathias and Crommelin, *Proc. Intern. Cong. Refrig.*, **41**, 89 (1924).

(35) Dodge and Davis, THIS JOURNAL, **49**, 610 (1927).

(36) Shearer, *Phys. Rev.*, [1] **17**, 469 (1903).

(37) Dewar, *Proc. Roy. Soc.* (London), **76A**, 325 (1906).

(38) Alt, *Ann. Physik*, **19**, 739 (1906).

(39) Hammick, *Phil. Mag.*, **44**, 509 (1922).

(40) Dana, *Proc. Am. Acad. Arts. Sci.*, **160**, 241 (1925).

results including a value calculated from our vapor pressure measurements are given in Table VII. The results of other observers are included.

The value obtained from the vapor pressure data is given no weight as compared to the direct determination.

The Entropy of Nitrogen.—A summary of the entropy calculation is given in Table VIII.

TABLE VIII

CALCULATION OF ENTROPY OF NITROGEN

0–10°K. Debye function $(h\nu/k) = 68$	0.458 E. U.
10–35.61°K., graphical	6.034
Transition 54.71/35.61	1.536
35.61–63.14°K., graphical	5.589
Fusion 172.3/63.14	2.729
63.14—Boiling point, graphical	2.728
Vaporization 1332.9/77.32	17.239
	36.31 ± 0.1 E. U.
Correction for gas imperfection assuming Berthelot gas	0.22
Entropy of ideal gas at boiling point	36.53 E. U.

The 0.22 E. U. correction for gas imperfection at the boiling point was obtained by combining Berthelot's equation of state with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$. This leads to the correction $\Delta S = R(27T_c^3P/32T^3P_c)$. The critical temperature and pressure were taken as $T_c = 126.0$°K., and $P_c = 33.5$ atm.[41,42]

The above correction is not as certain as might be desired, but the good agreement obtained between the indirect and direct heats of vaporization supports the use of Berthelot's equation.

The entropy for the ideal gas state may be compared with the value calculated from band spectra data.

$$S = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln P - \frac{5}{2}R - 7.267 + R\ln Q + RT\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \qquad (3)$$

$$Q = \Sigma p e^{-\epsilon/kT}$$

$$\epsilon_{\text{rotation}} = \left[B_e + \alpha\left(v + \frac{1}{2}\right)\right]m^2 + \left[D_e + \beta\left(v + \frac{1}{2}\right)\right]m^4$$

$$\epsilon_{\text{vibration}} = \omega_e\left(v + \frac{1}{2}\right) + \omega_e x_e\left(v + \frac{1}{2}\right)^2$$

The Raman spectrum data of Rasetti[43] give $B_e = 2.003$, $\alpha = -0.023$ (estimated by analogy with carbon monoxide and the relationship $\chi_e B_e/\alpha$ = const. due to Birge), $D_e = -5.773 \times 10^{-6}$ and $\beta = 8.61 \times 10^{-8}$. For the vibration constants Birge and Hopfield[44] give $\omega_e = 2359.61$ and $\omega_e\chi_e = -14.445$. All of the above constants have been converted to the conven-

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(41) Kamerlingh Onnes, Dorsmann and Holst, *Comm. Phys. Lab. Leiden*, 145b (1914).

(42) Pickering (Review), *Sci. Papers Bureau Stand.*, **21**, 608 (1926).

(43) Rasetti, *Phys. Rev.*, **34**, 367 (1929).

(44) Birge and Hopfield, *ibid.*, **29**, 212 (1927).

tional system which refers the molecular constants to the hypothetical state of zero vibration. To save labor in summing the rotational Boltzmann factors we have made use of the expression

$$Q = e^{hc(B/4)+(D/16)/kT}\left(\frac{kT}{hc}\right)\left[1+\frac{1}{12}\left(\frac{hc}{kT}\right)-\frac{2D}{B^2}\left(\frac{kT}{hc}\right)+\frac{12D^2}{B^4}\left(\frac{kT}{hc}\right)^2+\ldots\right] \qquad (4)$$[45]

and its derivative in evaluating the entropy. The results are given in Table IX. The Q given by Equation 4 has been reduced to one-half its value because of the molecular symmetry of nitrogen and the effect of nuclear spin has been eliminated.

TABLE IX

COMPARISON OF CALORIMETRIC AND SPECTROSCOPIC ENTROPIES OF NITROGEN

T, °K.	Spectroscopic	Calorimetric Actual gas	Calorimetric Corrected to ideal state
77.32	36.416	36.3 ± 0.1	36.5 E. U.
298.1	45.788	....	45.9

The "calorimetric" value at 298.1°K. was obtained by adding the spectroscopic increase to 36.5.

The agreement is very satisfactory and since the effect of nuclear spin has been neglected in the calculation, it indicates that the limiting high temperature nuclear spin entropy remains in the solid state below the temperatures of liquid hydrogen.

It also indicates that nitrogen is not rotating in the solid state in a manner similar to hydrogen. This is important since it supports the suggestion[46] that no substances, with the possible exception of some containing symmetrically located hydrogen atoms in the molecule, will possess entropy due to the effect of rotation in the solid state below the temperatures of liquid helium, thus complicating extrapolation. Absence of this rotation is assumed in the ordinary application of the third law.

Had nitrogen rotated in a manner similar to hydrogen the calorimetric entropy would have been decreased by $(1/3)R \ln 3 = 0.73$ E. U. This is computed as follows: the nuclear spin of the nitrogen atom is 1 Bohr unit of angular momentum. This leads to the spin statistical weights 6 and 3 for the even and odd rotational levels of the normal electronic state. Thus in the gas at extremely low temperatures three-ninths of the molecules would be unable to lose the rotational statistical weight associated with the state $j_{(\mathrm{rot.})} = 1$, thus leading to a zero point entropy of $(1/3)R \ln 3$. However, the experimental data show that the rotational weight of three has been lost in the solid state.

It is equally interesting that the lack of equilibrium between the two non-combining states of nitrogen is not altered by the solid. This is

(45) Giauque and Overstreet, THIS JOURNAL, 54, 1731 (1932).

(46) Giauque, *ibid.*, 52, 4816 (1930).

evident since, as mentioned above, the high temperature limiting spin entropy remains at low temperatures.

If all of the nitrogen molecules were changed to the form of lowest energy the entropy caused by nuclear spin would be $R \ln 6$, whereas the experimental facts correspond to $(6/9)\, R \ln 9 + (3/9)\, R \ln 9 = R \ln 9$, indicating the presence of the high temperature proportions of the two forms.

The Free Energy of Nitrogen.—From the band spectra data given above and the equation

$$\frac{F^\circ - E_0^\circ}{T} = -\frac{3}{2} R \ln M - \frac{5}{2} R \ln T + R \ln P + 7.267 - R \ln Q$$[47]

the values of $(F^\circ - E_0^\circ)/T$ have been calculated and are given in Table X. The values given in heavy type have been directly calculated. The others have been interpolated with a difference plot constructed by means

TABLE X

$-(F^\circ - E_0^\circ)/T$ FOR N_2 AND N

T, °K.	N_2	N	T, °K.	N_2	N
298.1	**38.834**	**31.655**	2200	53.239	**41.583**
300	**38.876**	**31.686**	2300	53.587	**41.804**
350	39.949	**32.452**	2400	53.922	**42.015**
400	**40.877**	**33.115**	2500	**54.246**	**42.219**
450	41.697	**33.700**	2600	54.558	**42.414**
500	**42.431**	**34.224**	2700	54.859	**42.601**
550	43.096	**34.697**	2800	55.150	**42.782**
600	43.705	**35.129**	2900	55.432	**42.957**
650	44.265	**35.527**	3000	**55.706**	**43.125**
700	44.786	**35.895**	3100	55.970	43.287
750	**45.272**	**36.238**	3200	56.228	43.445
800	45.729	**36.558**	3300	56.479	43.599
850	46.158	**36.859**	3400	56.723	43.747
900	46.566	**37.143**	3500	**56.960**	43.891
950	46.953	**37.412**	3600	57.191	44.032
1000	**47.322**	**37.667**	3700	57.417	44.168
1050	47.674	**37.909**	3800	57.637	44.302
1100	48.011	**38.140**	3900	57.852	44.432
1150	48.335	**38.361**	4000	**58.062**	**44.559**
1200	48.646	**38.572**	4100	58.267	44.682
1250	48.947	**38.775**	4200	58.468	44.803
1300	49.235	**38.970**	4300	58.664	44.921
1400	49.785	**39.338**	4400	58.855	45.036
1500	**50.301**	**39.681**	4500	**59.044**	**45.150**
1600	50.787	**40.001**	4600	59.228	45.261
1700	51.247	**40.303**	4700	59.409	45.369
1800	51.684	**40.586**	4800	59.586	45.475
1900	52.100	**40.855**	4900	59.760	45.580
2000	**52.497**	**41.110**	5000	**59.929**	**45.682**
2100	52.875	**41.352**			

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(47) Giauque, THIS JOURNAL, 52, 4808 (1930).

of comparison with the function for a rigid rotator and the harmonic oscillator. This method is so accurate that the interpolated values have about the same accuracy as the directly calculated ones.

The $(F^\circ - E_0^\circ)T$ for atomic nitrogen has also been included in Table X. The values below 3000°K. are taken from tables of this function for the elements in course of preparation by Roy Overstreet and one of us. Only the normal electronic ^{4}S state and to a small extent the ^{2}D levels at 19202 cm.$^{-1}$ and ^{2}P levels at 28808 cm.$^{-1}$ [48] are occupied below 5000°K.

The Dissociation of Nitrogen.—The heat of dissociation of the nitrogen molecule is known only very roughly. However, accepting the value 7.90 volts = 182,000 calories per mole[49] we may make a provisional calculation of the dissociation constant. When a more reliable value of ΔE_0° becomes available, it may very easily be combined with the values of $\Delta[(F^\circ - E_0^\circ)/T]$ for $N_2 = 2N$ which are given in Table XII.

$$\frac{\Delta F^\circ}{T} = -R \ln K = \Delta\left(\frac{F^\circ - E_0^\circ}{T}\right) + \frac{\Delta E_0^\circ}{T}$$

A few values of K based on the above value of ΔE° are also given in Table XII.

The Reaction $^1/_2$ N_2 + $^1/_2$ O_2 = NO.—Nitric oxide and oxygen have previously been investigated calorimetrically by Johnston and Giauque.[50,3b] Johnston and Chapman[51] have obtained the free energy of nitric oxide in connection with their calculation of the heat capacity of this substance and Johnston and Walker[52] have similarly obtained the free energy and dissociation of oxygen. The present work on nitrogen completes the information necessary for considering the free energy of formation of nitric oxide.

Thomsen and Berthelot have both measured the heat of formation of nitric oxide. From their data ΔE_0° may be calculated.

$$\Delta E_0^\circ = \Delta H_{\mathrm{T}} - \Delta(H_{\mathrm{T}}^\circ - E_0^\circ) = \Delta H_{\mathrm{T}} - \Delta\left(\frac{5}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right)$$

$$(H^\circ_{298.1} - E_1^\circ) \text{ for } N_2 = 2072.9$$

From the calculations of Giauque and Johnston[3b] $(H_{298.1}^\circ - E_0^\circ)$ for O_2 = 2070.4 and from Johnston and Giauque[50] $(H_{298.1}^\circ - E_0^\circ)$ for NO = 2216.8

$$\Delta(H_{298.1}^\circ - E_0^\circ) = 2216.8 - (2072.9/2) - (2070.4/2) = 145.1 \text{ calories per mole}$$

Berthelot[53] found ΔH = 21,600 cal. (20°) = 21,575 cal. (15°) per mole, ΔE_0° = 21,430. Thomsen[54] found ΔH = 21,575 cal. (20°) = 21,550 cal. (15°) per mole. ΔE_0° = 21,400. ΔE_0° may also be evaluated from determinations of the equilibrium constant.

$$\Delta E_0^\circ/T = -R \ln K - \Delta[(F^\circ - E_0^\circ)/T]$$

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(48) Compton and Boyce, *Phys. Rev.*, **33**, 145 (1929).

(49) Lozier, *Phys. Rev.*, **44**, 575 (1933) (dissociation of N_2 revised in proof).

(50) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

(51) Johnston and Chapman, *ibid.*, **55**, 153 (1933).

(52) Johnston and Walker, *ibid.*, **55**, 172 (1933).

(53) Berthelot, *Ann. chim. phys.*, **20**, 255 (1880).

(54) Thomsen, see "Thermochemistry," 1908.

In Table XI are given the various values of ΔE_0° obtained from the equilibrium amounts of nitric oxide resulting when air was heated.

TABLE XI

ΔE_0° FOR $^1/_2\,N_2 + {}^1/_2\,O_2 = NO$ FROM EQUILIBRIUM MEASUREMENTS AND SPECTROSCOPIC DATA

T, °K.	ΔE_0°	Author
1811	22150	Nernst[55]
1873	20110	Briner, Boner and Rothen[56]
1877	22550	Nernst and Jellinek[55]
2033	22700	Nernst
2195	22710	Nernst
2580	22800	Nernst–Finckh[55]
2675	23190	Nernst–Finckh

All of the values tabulated deviate considerably from those of Thomsen and Berthelot and in the case of Nernst and his co-workers the trend increases the uncertainty.

It seems best to adopt a value $\Delta E_0^\circ = 21{,}400$ based on the work of Thomsen and Berthelot. This is equivalent to $\Delta H_{298} = 21{,}500$ calories per mole for the formation of nitric oxide.

Using the above data the values of $\Delta[(F^\circ - E_0^\circ)/T]$, $\Delta F^\circ/T$ and K have been calculated for the reaction $^1/_2\,N_2 + {}^1/_2\,O_2 = NO$. The results are given in Table XII.

TABLE XII

FREE ENERGY OF FORMATION OF NITRIC OXIDE AND $\Delta[(F^\circ - E_0^\circ)/T]$ FOR THE DISSOCIATION OF NITROGEN

	$^1/_2\,N_2 + {}^1/_2\,O_2 = NO$			$N_2 = 2N$	
T, °K.	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$\Delta F^\circ/T$	$K = \frac{[NO]}{[N_2]^{1/2}\,[O_2]^{1/2}}$	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$k = [N]^2/[N_2]$
298.1	2.527	69.261	7.26×10^{-16}	24.476	1×10^{-128}
300	2.532	68.801	9.15×10^{-16}	24.496	
350	2.592	58.551	1.59×10^{-13}	24.955	
400	2.639	50.861	7.64×10^{-12}	25.353	
450	2.675	44.881	1.55×10^{-10}	25.703	
500	2.708	40.092	1.73×10^{-9}	26.017	1×10^{-74}
550	2.735	36.174	1.24×10^{-8}	26.298	
600	2.755	32.912	6.40×10^{-8}	26.653	
650	2.777	30.146	2.58×10^{-7}	26.789	
700	2.790	27.781	8.47×10^{-7}	27.004	
750	2.806	25.727	2.38×10^{-6}	27.204	
800	2.818	23.932	5.88×10^{-6}	27.387	
850	2.831	22.345	1.31×10^{-5}	27.560	
900	2.840	20.938	2.65×10^{-5}	27.720	
950	2.850	19.676	5.00×10^{-5}	27.871	
1000	2.859	18.541	8.86×10^{-5}	28.012	2×10^{-34}
1050	2.867	17.514	1.49×10^{-4}	28.144	
1100	2.877	16.578	2.38×10^{-4}	28.269	

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(55) Nernst, *Z. anorg. Chem.*, **49**, 213 (1906).

(56) Briner, Boner and Rothen, *J. chim. phys.*, **23**, 788 (1926).

TABLE XII (*Concluded*)

T, °K.	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$\Delta F^\circ/T$	$K = \frac{[NO]}{[N_2]^{1/2}\,[O_2]^{1/2}}$	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$k = [N]^2/[N_2]$
1150	2.879	15.730	3.65×10^{-4}	28.387	
1200	2.888	14.945	5.41×10^{-4}	28.498	
1250	2.892	14.228	7.76×10^{-4}	28.603	
1300	2.897	13.565	1.08×10^{-3}	28.705	
1400	2.906	12.380	1.97×10^{-3}	28.891	
1500	2.915	11.352	3.30×10^{-3}	28.061	4×10^{-21}
1600	2.922	10.453	5.19×10^{-3}	29.215	
1700	2.929	9.659	7.74×10^{-3}	29.359	
1800	2.936	8.953	1.10×10^{-2}	29.488	
1900	2.943	8.320	1.52×10^{-2}	29.610	
2000	2.948	7.752	2.02×10^{-2}	29.723	4×10^{-14}
2100	2.954	7.236	2.62×10^{-2}	29.829	
2200	2.959	6.768	3.32×10^{-2}	29.927	
2300	2.963	6.341	4.11×10^{-2}	30.021	
2400	2.967	5.950	5.01×10^{-2}	30.108	
2500	2.970	5.590	6.00×10^{-2}	30.192	5×10^{-10}
2600	2.974	5.257	7.09×10^{-2}	30.270	
2700	2.977	4.949	8.29×10^{-2}	30.343	
2800	2.980	4.663	9.57×10^{-2}	30.414	
2900	2.982	4.397	1.09×10^{-1}	30.482	
3000	2.985	4.148	1.24×10^{-1}	30.544	3×10^{-7}
3100	2.989	3.914	1.40×10^{-1}	30.604	
3200	2.991	3.697	1.56×10^{-1}	30.662	
3300	2.994	3.491	1.73×10^{-1}	30.719	
3400	2.997	3.297	1.90×10^{-1}	30.771	
3500	2.999	3.115	2.09×10^{-1}	30.822	2×10^{-5}
3600	3.001	2.943	2.27×10^{-1}	30.873	
3700	3.003	2.781	2.47×10^{-1}	30.919	
3800	3.003	2.629	2.66×10^{-1}	30.967	
3900	3.003	2.484	2.86×10^{-1}	31.012	
4000	3.003	2.347	3.07×10^{-1}	31.056	7×10^{-4}
4100	3.005	2.215	3.28×10^{-1}	31.097	
4200	3.005	2.090	3.49×10^{-1}	31.138	
4300	3.005	1.972	3.71×10^{-1}	31.178	
4400	3.006	1.858	3.93×10^{-1}	31.217	
4500	3.004	1.752	4.14×10^{-1}	31.256	1.0×10^{-2}
4600	3.004	1.648	4.36×10^{-1}	31.294	
4700	3.002	1.551	4.58×10^{-1}	31.329	
4800	3.002	1.456	4.81×10^{-1}	31.364	
4900	3.002	1.365	5.03×10^{-1}	31.400	
5000	3.003	1.277	5.26×10^{-1}	31.435	8×10^{-2}

Table XIII summarizes the observed and calculated values of the equilibrium constant for the reaction $^1/_2\,N_2 + {}^1/_2\,O_2 = NO$. The measurements were made by determining the amount of NO formed in air at high temperatures. In calculating the equilibrium constants the composition of dry air was taken as 78.03% oxygen and 20.99% nitrogen.(57)

(57) "I. C. T.," Vol. I, p. 393.

TABLE XIII

OBSERVED AND CALCULATED EQUILIBRIUM CONSTANTS FOR THE FORMATION OF NITRIC OXIDE

T, °K.	%NO	$K_{\text{obs.}}$	$K_{\text{calcd.}}$	Observer
1811	0.37	0.0093	0.0114	Nernst[55]
1873	.79	.0198	.0140	Briner, Boner and Rothen[56]
1877	.42	.0104	.0142	Nernst and Jellinek[55]
2033	.64	.0160	.0221	Nernst
2195	.97	.0243	.0328	Nernst
2580	2.05	.0523	.0687	Nernst-Finckh[55]
2675	2.23	.0580	.0798	Nernst-Finckh

The observations differ quite appreciably from the calculated values. However, the agreement is perhaps all that might be expected when the difficulty of experiment at such high temperatures is considered. A redetermination of the heat of formation of nitric oxide seems very desirable. Such a determination with the advantage of modern technique would, when combined with the tabulated values of $\Delta[(F^\circ - E_0^\circ)/T]$, yield equilibrium constants with an insignificant error.

We wish to express our thanks to Dr. R. W. Blue for assisting with the experimental work.

Summary

The heat capacity of the two crystalline forms and of liquid nitrogen has been measured from 15°K. to the boiling point.

The transition, melting and boiling points are 35.61, 63.14 and 77.32°K., respectively.

The calorimetric heats of transition, fusion and vaporization (at 760 mm.) are 54.71, 172.3 and 1332.9 calories per mole, respectively.

From the calorimetric measurements and the third law of thermodynamics the entropy of nitrogen at its boiling point was found to be 36.3 ± 0.1 E. U. A 0.2 E. U. correction for gas imperfection, using Berthelot's equation, gives 36.5 E. U. as the entropy of the ideal gas at 77.32°K.

The entropy was also calculated from band spectrum data. At 77.32°K. the value was found to be 36.416 E. U. in excellent agreement with the experimental 36.5. At 298.1°K., $S = 45.788$ calories per degree per mole. None of the above entropy values contain the amount of entropy due to nuclear spin. The absolute entropy at 298.1°K. is $45.788 + R \ln 9 = 50.154$ E. U.

It has been concluded that, although lack of equilibrium between the two series of "non-combining" states of nitrogen persists into the solid state at 13°K., no molecular rotation remains in the solid at this temperature, as is the case in hydrogen.

The vapor pressure of solid and liquid nitrogen has been measured and the results have been represented by the equations: solid nitrogen 54.78 to 63.14°K., $\log_{10} P \text{ (cm.)} = -(381.6/T) + 7.41105 - 0.0062372\,T$; liquid

nitrogen 63.14 to 78.01°K., $\log_{10} P$ (cm.) $= -(339.8/T) + 6.71057 - 0.0056286\ T$.

The free energies and equilibrium constants for the reactions $^1/_2\ N_2 + {}^1/_2\ O_2 = NO$ and $N_2 = 2N$ have been calculated to 5000°K. with the assistance of spectroscopic data. The free energy of formation of nitric oxide was found to be $\Delta F^{\circ}_{298.1} = 20{,}650$ calories per mole.

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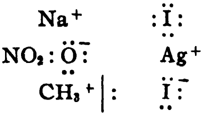
The Electronic Structure of Inorganic Complexes

BY WILLIAM ALBERT NOYES

Soon after Arrhenius proposed his theory of ionization a distinction was made between "heteropolar" and "homopolar" compounds. This corresponds closely to our distinction between ionic and covalent compounds. Chemists have very generally supposed that ionic compounds react very rapidly and that covalent compounds react slowly or not at all. Professor Kahlenberg, many years ago, showed the illusory nature of such a method of distinguishing the two classes of compounds but, because his views of ionization were considered heterodox, the facts which he stated have been too generally disregarded.

The fact that covalent methyl iodide reacts with silver nitrate in an alcoholic solution almost or quite as rapidly as ionic sodium iodide demonstrates that the two classes of compounds cannot be distinguished by the speed of their reactions.



$$\begin{array}{lc} Na^+ & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{I}}: \\ NO_2:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^- & Ag^+ \\ CH_3{}^+ \,|\, : & \overset{\cdot\cdot}{\underset{\cdot\cdot}{I}}:^- \end{array}$$

Both reactions are ionic but the positive methyl has only an ephemeral existence.

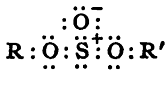
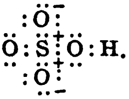
Instead of speed of reactions we must rely on other properties to distinguish between covalences and ionic valences. The most important of these are conductivity in solutions, molecular weights in solutions, Sugden's parachor, optical activity and, especially, electronic structure. The last can frequently be inferred with a high degree of probability.

That there is an absolute balance between the positive charge of the nucleus of an atom and the negative charges of the electrons surrounding the nucleus is universally accepted by chemists and physicists. That every ion consisting of a single atom has a stable group of electrons the sum of whose negative charges overbalances or underbalances the positive charge of its nucleus and that in every complete molecule the sum of the charges of the electrons balances the sum of the charges of the nuclei, are universally accepted.

It has not been so generally accepted that in every complex ion its positive or negative charge is due to some atom or atoms the charge of whose nucleus (or kernel) is not balanced by the electrons immediately surrounding it, counting the pair of electrons of a covalence as equivalent to a single unshared electron; conversely, that any atom the charge of whose nucleus is not so balanced is an ion or part of a complex ion. In the light of what follows, it seems reasonable to consider these statements as forming a hypothesis which deserves serious consideration until someone can furnish a well-established exception.

One reason why this relation has not been generally recognized is because chemists have failed to see clearly the sharp distinction between "potentially polar"[1] covalences and fully polar (or ionic) valences. This distinction was first vaguely recognized in 1901 when Noyes and Lyon[2] supposed that chlorine molecules reacting with ammonia separate into chloride ions and positive chlorine atoms; by Stieglitz,[3] who pointed out that hypochlorous acid is formed by replacing the hydrogen of water by positive chlorine; and by Lapworth,[4] who showed a similar conduct for bromine.

Potential polarity was shown more clearly[5] by the quantitive decomposition of nitrogen trichloride by hydrochloric acid and by explaining the positive potential polarity of the chlorine of nitrogen trichloride as due to the fact that the nitrogen kernel has only two electrons and the negative potential polarity of the chlorine of phosphorus trichloride as due to the fact that the kernel of the phosphorus atom has ten electrons.[6]

Potentially polar atoms united by a covalence often give an electrical moment to the molecule containing them and such molecules are called "polar" by many chemists and physicists. Since this usage is quite general, the suggestion that the term polar should be used only for ions[7] seems to have little chance of success and may as well be abandoned. In that case, however, the term "semi-ionic" should be used instead of "semi-polar" for the oxygen of the optically active sulfinates,  $\mathrm{R}:\underset{..}{\ddot{\mathrm{O}}}:\overset{:\ddot{\mathrm{O}}:^{-}}{\underset{..}{\mathrm{S}}^{+}}:\underset{..}{\ddot{\mathrm{O}}}:\mathrm{R'}$, the amine oxides, $\mathrm{R_3\overset{+}{N}}:\underset{..}{\ddot{\mathrm{O}}}:^{-}$ and sulfuric acid,  $\mathrm{H}:\underset{..}{\ddot{\mathrm{O}}}:\overset{:\ddot{\mathrm{O}}:^{-}}{\underset{:\underset{..}{\ddot{\mathrm{O}}}:^{-}}{\ddot{\mathrm{S}}^{++}}}:\underset{..}{\ddot{\mathrm{O}}}:\mathrm{H}$.

The disadvantage of the word "polar" as applied to covalent compounds is that we have all degrees of polarity from that of the hydrogen of

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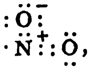
(1) W. A. Noyes, *Z. physik. Chem.*, **130**, 329 (1927).
(2) Noyes and Lyon, THIS JOURNAL, **23**, 463 (1901).
(3) Stieglitz, *ibid.*, **23**, 797 (1901).
(4) Lapworth, *J. Chem. Soc.*, **79**, 267 (1901).
(5) W. A. Noyes, THIS JOURNAL, **42**, 2167, 2173 (1920).
(6) Noyes and Noyes, "Modern Alchemy," p. 107.
(7) W. A. Noyes, *Z. physik. Chem.*, **130**, 327 (1927).

hydrocarbons to that of the iodine of methyl iodide. The only sharp line that can be drawn is the point where the pair of electrons ceases to be *shared*—in other words, when the two atoms joined by a covalence become ions.

Sidgwick in his classical book on "The Electronic Theory of Valency" points out that covalences may be formed in two ways. In the first, each atom furnishes one of the pair of electrons. Each nitrogen atom furnishes its three valence electrons and each hydrogen atom furnishes one electron in the synthesis of ammonia. In the second, one atom or molecule, which he calls the "donor," furnishes the two electrons for the covalence and the other, which he calls the "acceptor," furnishes none.

In the first case the product is electrically neutral because each atom exchanges a single unshared electron for the covalence. The resulting molecule may be "potentially polar" and have an electrical moment but it will never be an ion unless one of the constituents was an ion. In the second case the donor, which exchanges a pair of unshared electrons for a covalence, increases its positive ionic valence by one. The acceptor increases its negative ionic valence by one.

Sidgwick has recognized that the donor increases its positive character and that the acceptor increases its negative character but he has hesitated to accept this as a unit change in the ionic valence of each atom because the electrons of a covalence are usually not shared equally by the two atoms. He has noticed that the group containing the donor acquires a positive charge of one unit but has not seemed to see that, in effect, the donor increases its valence by two; one covalence and one ionic valence. The acceptor, on the other hand, increases its negative ionic valence by one, becoming electrically neutral if it was a positive ion, or acquiring a negative ionic valence of one if it was electrically neutral. It also acquires a covalence.

On p. 114 he makes the confusing, if not positively erroneous, statement that, "In order to become quadrivalent nitrogen must, as we know, lose an electron." The nitrogen of methylammonium chloride, which he is considering, is quinquivalent, not quadrivalent, since it has four covalences and one positive ionic valence. The methyl which unites with the nitrogen must do so as a positive methyl ion, with a carbon atom having only six electrons. In uniting with the unshared electrons of the nitrogen this positive methyl becomes electrically neutral, increasing its negative ionic valence by one. The only well-known compound in which nitrogen is really quadrivalent is nitrogen dioxide,  $\begin{array}{l}\;\;:\ddot{O}:^{-}\\ \cdot\ddot{N}\overset{+}{\vdots}:\underset{\cdot\cdot}{\ddot{O}}\end{array}$, in which the nitrogen has three covalences and one positive ionic valence.

Sidgwick has performed a very great service by explaining the "coordination" of inorganic complexes as due to covalences. This unifies the electronic theory by applying it to all elements and to all classes of compounds. His definition of a "coördinate link" as one in which one of the atoms furnishes the pair of electrons for a covalence is not satisfactory, however. The covalence which holds the fourth hydrogen atom of the ammonium ion is identical with the other three covalences of the group. The "covalent link" when it has been formed does not differ from other covalences except that the number of coördinated covalences may exceed the number of normal covalences for the atom which accepts them. This is an important principle of Werner's system.

Sidgwick has given rules for determining the ionic valence of an inorganic complex. A simpler system can be based on the relationship between the changes in the ionic valences of donors and acceptors stated above, the coördination number of Werner, which is also the number of covalences around the central atom, six for cobaltic cobalt, four for platinous platinum, six for platinic platinum, etc., and the ionic valence of the central atom, three for cobaltic cobalt, two for platinous platinum, four for platinic platinum, etc.

The application of these principles will be easily understood from the following illustrations. For a part of these Sidgwick has not recognized the principle of "donor" and "acceptor."

In $\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot +}{\mathrm{F}}}:\overset{-}{\mathrm{H}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:$ the hydrogen atom with two covalences is acceptor from the first fluorine atom and negative. The first fluorine atom, as donor, is positive. The second fluorine atom is electrically neutral with six unshared electrons and one covalence. This formula helps us to understand the low ionization constant of hydrofluoric acid.

In the $\mathrm{H}:\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}\overset{+}{:}\mathrm{H}$ ion, the nitrogen as donor is positive and the hydrogen ion, increasing its negative charge by one, algebraically, is neutral.

In the formation of trimethylsulfonium iodide, $\mathrm{CH_3}:\underset{\underset{\mathrm{CH_3}}{\cdot\cdot}}{\overset{\overset{\mathrm{CH_3}}{\cdot\cdot}}{\mathrm{S}}}:^{+},\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{I}}}:^{-}$, from dimethyl sulfide and methyl iodide the iodide ion in separating from the methyl takes both the electrons of the covalence, leaving the methyl as a positive ion. The positive methyl, as acceptor from the sulfur atom of the dimethyl sulfide, becomes neutral and the sulfur, as donor, positive.

In the fluosilicate ion, $\begin{array}{ccc} & \mathrm{F} & \\ & \cdot\cdot & \\ \mathrm{F}: & & :\mathrm{F}^{-} \\ & \mathrm{Si} & \\ \mathrm{F}: & & :\mathrm{F} \\ & \cdot\cdot & \\ & \mathrm{F} & \end{array}$, the kernel of the silicate atom, which has four positive charges, may be considered as the acceptor for six fluoride ions. The six negative charges convert it to a bivalent negative ion and each fluoride ion as a donor becomes neutral.

In the Werner series, $[Co(NH_3)_6]^{+++}\cdot 3Cl^-$, $\left[\begin{matrix} & Cl \\ Co & \\ & (NH_3)_5\end{matrix}\right]^{++}\cdot 2Cl^-$, $\left[\begin{matrix} & Cl_2 \\ Co & \\ & (NH_3)_4\end{matrix}\right]^{+}\cdot Cl^-$, $\left[\begin{matrix} & Cl_3 \\ Co & \\ & (NH_3)_3\end{matrix}\right]^{0}$, $\left[\begin{matrix} & Cl_4 \\ Co & \\ & (NH_3)_2\end{matrix}\right]^{-}\cdot K^+$, $\left[\begin{matrix} & Cl_5 \\ Co & \\ & (NH_3)\end{matrix}\right]^{=}\cdot 2K^+$, $[CoCl_6]^{\equiv}\cdot 3K^+$, the cobalt kernel, which has three positive ionic charges, is acceptor, in each compound, of six covalences from chloride ions or from molecules of ammonia, changing it to a trivalent negative ion. As donor each molecule of ammonia becomes a positive ammonium ion and each negative chloride ion becomes neutral. A little consideration will show that this gives the resultant complexes the charges shown in the formulas.

In other compounds, when molecules of water enter the complexes they become positive oxonium ions.

The negative nitrite and cyanide ions may enter the complexes in the same manner as the chloride ion does, becoming electrically neutral and assuming the forms, $R:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{N}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$ and $R:C:::N:$. Since the trivalent nitrogen atom of each group has a pair of unshared electrons, these groups may rearrange giving nitro or isocyanide groups with the structures, $R:\overset{\overset{\cdot\cdot}{:O:}^{-}}{\overset{\cdot\cdot}{N}}\overset{+}{:}:\overset{\cdot\cdot}{O}$ and $R:\overset{+}{N}:::\overset{-}{C}:$ or $R:\overset{\cdot\cdot}{N}::C:$. The carbon in the last formula is bivalent, which might explain the preparation of carbon monoxide from potassium ferrocyanide and concentrated sulfuric acid.

In potassium chloroplatinate, $[PtCl_6]^{=}\cdot 2K^+$, the quadrivalent platinic ion becomes a bivalent negative ion. Platinum furnishes a series of complexes similar to those of coblat, with the differences caused by the quadrivalent platinum.

Summary

On the basis of Sidgwick's assumption that the "coördinated" ions and molecules of the Werner complexes are "donors" and the central metallic ions are "acceptors," combined with the principle that a donor increases its positive ionic valence by one and that an acceptor increases its negative ionic valence by one, a simple explanation of the ionic charges of the complexes is given.

The importance of the distinction between the "potentially polar" covalences and ionic valences is discussed.

The possibility of the rearrangement of the negative nitrite and cyanide ions to positive nitro and isocyanide groups is explained.

URBANA, ILL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The Collision Areas of 1,3,5-Mesitylene and of the Most Highly Branched Heptanes

BY W. A. EVERHART, W. A. HARE[1] AND EDWARD MACK, JR.

A method previously given for matching molecule collision areas determined[2] experimentally by gaseous viscosity measurements with collision areas of probable models made to scale has now given consistently such successful results that it would seem that this type of approach could well be generalized to attack various problems of unknown or disputed spatial configuration of organic molecules, with the expectation of obtaining satisfying solutions. While, in the present paper, no attempt will be made to gain a decision between any disputed structures, some further evidence of the general trustworthiness of the method will be presented. We have chosen for examination two molecules which possess quite different collision areas, and which exhibit rather interesting features of structure in their spatial configuration, namely, 1,3,5-mesitylene and the most highly branched carbon chain of the heptane isomers (2,2,3-trimethylbutane).

First the data and the mathematical reduction of the data will be given, followed by a discussion of the results.

Experimental Procedure and Data

The viscosities of the two vapors were determined experimentally at several temperatures with the same apparatus and in precisely the manner already described.[2] The boiling points of mesitylene and of the heptane, the latter prepared synthetically according to the method[3] used by Edgar, Calingaert and Marker,[4] were, respectively, 164.5 and 80.2° (at 752 mm).

TABLE I

VISCOSITY DATA AND COLLISION AREA FOR MESITYLENE

Temp., °C.	η	η_0	Sutherland constant	Collision area (sq. Å.)
100.4[a]	$0.725^b \times 10^{-4}$	0.746×10^{-4}		43.03
150.4	$.807^b \times 10^{-4}$	$.834 \times 10^{-4}$	136.3	42.2
200.0	$.873^b \times 10^{-4}$	$.907 \times 10^{-4}$		42.1
			Av.	42.4

[a] This measurement at 100.4° was made by Dr. Ralph M. Melaven.

[b] The density of the liquid mesitylene at 65°, the temperature at which the mesitylene vaporized during the transpiration, was taken as 0.8265 [Perkin, *J. Chem. Soc.*, **69**, 1193 (1896)].

Calibration of the capillary with dry air gave the following results for the viscosity of air: at 24.2°, 182×10^{-6}; at 125°, 226×10^{-6}; at 200°, 256×10^{-6}.

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(1) Du Pont Fellow at The Ohio State University, 1931–1932.

(2) Melaven and Mack, THIS JOURNAL, **54**, 888 (1932).

(3) Chavanne and Lejeune, *Bull. soc. chim. Belg.*, **37**, 98 (1922).

(4) Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1483 (1929).

TABLE II

VISCOSITY DATA AND COLLISION AREA FOR 2,2,3-TRIMETHYLBUTANE

Temp., °C.	η	η_c	Sutherland constant	Collision area, sq. Å.
70.3[b]	$0.729^a \times 10^{-4}$	0.734×10^{-4}		
101.1	.763[a]	.769	257	31.10
132.2	.820[a]	.827		31.08
176.1	.892[a]	.900		31.20
262.1	1.037[a]	1.048		31.10
				Av. 31.12

[a] The density of the liquid heptane at 22.5°, the temperature at which the heptane vaporized during transpiration, was taken as 0.6879 [Edgar and Calingaert, THIS JOURNAL, 51, 1544 (1929)].

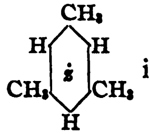
[b] In calculating the value of *C*, the Sutherland constant, the viscosity obtained at 70.3° was not used. High values for η are frequently found for temperatures close to the boiling point and have been ascribed to inexactness of the Sutherland equation at low temperatures [Rankine, *Proc. Roy. Soc.* (London), A88, 575 (1913)].

The experimental conditions were chosen so that the transpiration of the vapors through the capillary was slow enough to ensure viscous, and not permit turbulent, flow. The viscosities η at the several temperatures were calculated with Meyer's transpiration formula, as before, and were corrected for slip, η_c. Then the Sutherland constants were computed graphically and the collision areas calculated by means of Chapman's equation.

Discussion

Mesitylene.—For the shadow-graphic estimation of the average cross-sectional area of the mesitylene molecule, a model was made to scale (1 inch = 1 Å.), consisting of a flat graphite ring of six carbon atoms with diameters 1.42 Å. Three methyl groups were attached in the plane of the ring in the 1,3,5-positions. Three hydrogen atoms were also attached in the 2,4,6-positions, although as far as effect on the collision area is concerned the three hydrogens were completely buried underneath the larger methyl groups. The hydrogen atoms of the methyl groups were attached at tetrahedral angles, at internuclear C–H distances of 1.08 Å., and with a hydrogen domain radius of 0.72 Å. because of the probability that three hydrogen atoms on the average on one molecule bump three hydrogen atoms of another molecule in collision. The discussion of this point has already been given,[2] and in the construction of these models it is our consistent practice to assign hydrogen atom domain radii of 0.50, 0.65, 0.72 or 0.78 Å. when one, two, three or four hydrogen atoms, respectively, on a molecule partake in the collisional impact. Furthermore, since Pauling[5] has shown that the rotation of methyl groups around the C–C bond is easily excited, it is extremely probable that all three methyl groups on this molecule are spinning at the temperatures involved. A consideration of

(5) Pauling, *Phys. Rev.*, 36, 430 (1930).

the equipartition of energy principle and the moment of inertia of the methyl group, together with the average velocity of approach of bombarding molecules, shows that the methyl groups are undoubtedly spinning rapidly enough to present themselves as total rings of revolution. Similarly, it can be demonstrated that the spin of the molecule as a whole about the *z* axis, which passes through the center of the ring, and is perpendicular to the plane of the ring,  is rapid enough to produce effectively an almost total ring of revolution; although the spins about the other two rectangular axes, *x* and *y*, perpendicular to the *z* axis, are not sufficiently rapid to produce a *sphere* of revolution or in fact to affect the target area appreciably. The model of the electronic dome domain, the presence of which is due to the unsaturation of the benzene ring, was also attached to each face of the ring. The dome size (gas kinetic radius 2.0 Å.)[6] is, however, too small in comparison with the methyl rings to play anything but a minor part in producing the observed average collision area.

The average shadow area of this model ring of revolution (about the *z* axis) was then computed at forty-two different positions, separated from one another by approximately equal angles, as previously described.[2] The average collision area thus predicted for the molecule is 42.7. This is certainly in good agreement with the experimentally determined collision area of Table I.

Heptane, 2,2,3-Trimethylbutane.—Figure 1 shows an end view of the model of the branched heptane molecule. The spinning methyl groups M_1, M_2 and M_3 are attached at tetrahedral angles to carbon atom C_1. Directly behind C_1 is another carbon atom C_2 (not shown in drawing) to which are attached methyl groups M_4 and M_5 and hydrogen atom H, all at tetrahedral angles. A consideration of the moments of inertia about three different spin axes of the molecule taken as a whole, shows that the frequency of spin, compared with the average velocity of approach of bombarding molecules, is not sufficiently great to allow the molecule to present itself either as a sphere or as a cylinder of revolution. This justifies the procedure, then, of finding the average cross-sectional area of the static model by the shadow-graphic method.

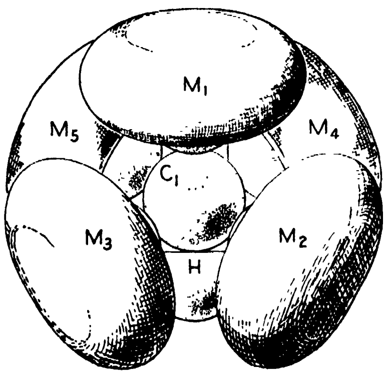


Fig. 1.

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(6) Mack, This Journal, 54, 2141 (1932).

The average of forty-two different positions gives 29.5, on the assumption that *three* hydrogen atoms on each colliding molecule partake in an average collision. If *four* hydrogen atoms collide, on the average, the model collision area is 30.8. This again is in quite good agreement with the experimentally determined value of 31.1, in Table II.

In a previous paper[2] the collision area of the *n*-heptane molecule has been determined experimentally to be 26.7 sq. Å., and by an application of the shadow-graphic method the conclusion was reached that the *n*-chain is coiled up into a tight helix. In the present case the molecule is already bunched up by its structure into a compact, roughly spherical form, and its five spinning methyl groups give it a considerably larger collision area than that of the helical *n*-heptane. While the methyl groups themselves undoubtedly are spinning, it is not probable that the C_1 and C_2 carbon atoms can rotate on the bond which connects them. This is due to the size of, and manner of placement of, the methyl groups, the steric hindrance of which would prevent any such rotation. The same situation would exist in hexamethylethane.

Thus one would predict for these molecules, made up of isopropyl and tertiary-butyl groups, the same sort of isomerism recently observed for diphenyl, and one could easily proceed to the prediction of the possible isomers to be found, for example, for the di-halogen substitution products.

Summary

The viscosities of the vapors of 1,3,5-mesitylene and 2,2,3-trimethylbutane have been measured over a considerable temperature range, and the Sutherland constants and collision areas, respectively, 136.3 and 257, and 42.4 and 31.1 sq. Å., have been calculated from the data.

The shadow-graphically computed collision areas of the models made to scale, are 42.7 for mesitylene and 29.5 (or 30.8) for the heptane. These good matches between calculated and observed results are submitted as still further evidence for the reliability of this general method of determining spatial configuration of organic molecules.

A type of space isomerism similar to that found in diphenyl is predicted for 2,2,3-trimethylbutane and for hexamethylethane.

COLUMBUS, OHIO RECEIVED OCTOBER 25, 1933
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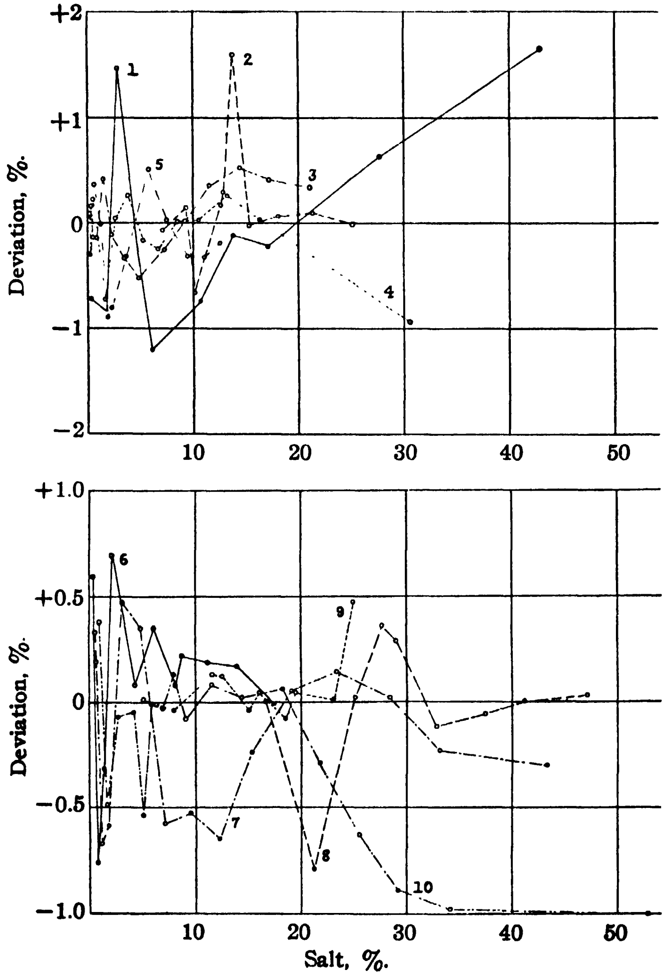
Notes

Ternary Systems: Water, Pyridine and Salts at 25°

By P. M. Ginnings, Bailey Webb and Emi Hinohara

In a previous study of the ternary systems water, aliphatic alcohols and salts,[1] empirical equations were obtained representing with reasonable accuracy the solubilities of the salts in aqueous alcoholic solutions. For purposes of comparison, we have now made similar measurements and have derived corresponding equations for systems in which pyridine is



Deviation charts of experimental values of weight per cent. of pyridine from values calculated using the empirical equations.

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(1) Ginnings, Herring and Webb, This Journal, 55, 875–878 (1933).

employed instead of the aliphatic alcohols. Pyridine resembles the aliphatic alcohols (namely, isopropanol and tertiary butanol) in its complete miscibility with water, but is very unlike them in its chemical properties.

The methods and experimental procedure were essentially identical with those used previously (1) and if details are desired, reference should be made to the previous paper. The authors feel that the results obtained are not in error more than one per cent. in any case; and that the results can be reproduced with less deviation than this by a person experienced in this type of work. Plait points and percentage deviations are given in the following table and charts. C. P. pyridine, d_4^{20} 0.9812, was used throughout this investigation, without purification.

Empirical equations were derived to fit these data. It was found that the exponential equation

$$\text{(A)} \quad y = a + b(10)^{-cx}$$

where y = weight percentage of pyridine, x = weight percentage of salt, and a, b and c are arbitrary constants, gave the best fit in practically all cases. However, in the salt-rich solutions of ammonium sulfate and sodium chloride, the power equation

$$\text{(B)} \quad y = a + bx^{-c}$$

gave a better fit.

The values of the constants and the limiting values of x are given in the accompanying table.

TABLE I

Dev. curve	Salt	Pyridine-rich section Eq.	a	b	c	Limit for "x"	Salt-rich section Eq.	a	b	c	"x" at plait point
6	Na_2SO_4	A	17.2	43.5	0.1754	4.8	A	1.20	64.4	0.0975	4.97
9	KCl	A	−24.0	102.6	.0238	13.5	A	0	175.8	.0626	11.77
4	KF	A	9.8	57.45	.1402	4.4	A	1.17	88.1	.1332	4.11
5	$MgSO_4$	A	46.95	37.0	2.060	0.6	A	0	51.9	.0687	5.31
8	$NaNO_3$	A	−45.9	153.6	.01234	35.8	A	1.62	45960	.1047	29.93
3	Na_2CO_3	A	23.90	38.10	.3365	3.0	A	0.20	57.2	.1126	3.22
7	$Na_2S_2O_3$	A	22.65	48.35	.1527	6.1	A	.80	79.4	.0744	5.76
10	K_2CO_3	A	8.0	50.7	.0974	4.2	A	1.31	68.9	.0983	4.92
1	$(NH_4)_2SO_4$	A	22.8	47.15	.1682	5.9	B	−4.35	251.6	1.176	5.90
2	NaCl	A	17.1	104.7	.0722	12.5	B	0	96380	3.220	12.46

DEPARTMENT OF CHEMISTRY
GREENSBORO COLLEGE
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RECEIVED MAY 29, 1933
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A New Relation between Viscosity, Vapor Pressure and Density

BY FRANK HOVORKA

In attempting to make some useful calculations between the viscosity and the vapor pressure of liquids, it was found that the empirical equation $S = \eta P^{1/4} d^{1/2}$, where η is the viscosity, P the vapor pressure, d the density, and S a constant characteristic of the substance under consideration, holds very closely for a great many organic liquids.

In Table I are represented at random a few of the substances of different homologous series for which the constant S was calculated. It may be noticed in Table I that the variation of constant S is very small, and falls probably in many cases within the experimental error of the determination of the three properties involved in the calculation. About the same variation was found in the case of thirty or more other substances for which the constant S was calculated. In taking the values of S for aliphatic esters from methyl formate to methyl isobutyrate it was found that the constant S is approaching a constant value characteristic of that series. The same is indicated for the saturated hydrocarbons. If the value of S, for instance, obtained for ethyl acetate is used for any higher ester in calculating the density, vapor pressure, or the viscosity, the error in most of the cases proved to be very small. These same effects have been noticed for other series which thus far have been calculated only approximately due to the lack of experimental data.

TABLE I

VALUES OF CONSTANT S AT DIFFERENT PRESSURES

V. p., mm.	$CHCl_3$	$(C_2H_5)_2O$	n-C_6H_{14}	n-C_7H_{16}	$(CH_3)_2CO$	$CH_3COOC_3H_7$	$C_3H_7COOCH_3$
100	0.0244	0.0934	0.00868	0.00855	0.0108	0.0124	0.0124
200	.0244	.0936	.00870	.00857	.0108	.0124	.0124
400	.0244	.0938	.00871	.00859	.0109	.0124	.0123
600	.0243	.0939	.00870	.00859	.0110	.0123	.0123

An attempt is being made to evaluate the constant S independently.

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A Quantitative Study of the Lanthanum-Neodymium Separation

BY P. W. SELWOOD

The writer had occasion for another investigation to prepare a considerable quantity of a lanthanum-neodymium mixture and, during recovery of this material, opportunity has been taken to make quantitative measurements on eight separation procedures including all standard methods available for the cerium group. The fractions were analyzed by means of their magnetic susceptibilities. The original mixture contained 29.6% Nd. Six-gram samples of the mixed oxides were taken in each case.

While the above results have not necessarily been obtained through the optimum conditions for all or any one of the separations, yet Prandtl's basic ammonia separation is shown to be definitely the most efficient of the methods as described in the literature. In actual practice it is frequently found that a reversal of the solubility order facilitates rapid purification. The oxalate method, which is the most efficient of the solubility

TABLE I

SUMMARY ON LANTHANUM–NEODYMIUM SEPARATIONS

Method	Ppt. (g. oxide)	% Nd in ppt.	% Nd in in filtrate	More soluble element
Sulfate[1]	2.9	24	35	Nd
Oxalate[1]	3.1	43	16	La
Alkali carbonate[1]	5.3	25	62	Nd
NH_4 double nitrate[1]	3.5	20	44	Nd
Basic magnesia[1]	1.2	61	22	La
Basic ammonia[2]	2.3	59	11	La
Basic urea[3]	1.9	43	23	La
Basic electrolytic[4]	1.0	60	24	La

procedures, has unfortunately the same serial solubility order as the basic precipitations. The ammonium double nitrate seems to be the next best choice.

(1) Procedure as in Little, "Textbook of Inorganic Chemistry" (Friend), Griffin, London, 1917.

(2) This is Prandtl's modification, using $Cd(NO_3)_2 + NH_4NO_3$, of the straight ammonium hydroxide basic separation [Prandtl and Hüttner, *Z. anorg. allgem. Chem.*, **136**, 289 (1924)].

(3) Six grams of mixed oxides was converted to nitrates, almost neutralized with ammonium hydroxide and diluted to 1 liter. Ten grams of urea was added and the mixture was kept at the boiling point for four hours. The precipitate formed was quite granular. The writer is indebted to Professor H. H. Willard of the University of Michigan for suggesting this method. He understands that Professor Willard has made an exhaustive study of the use of urea as an analytical reagent for group three elements.

(4) Dennis and co-workers, THIS JOURNAL, **37**, 131, 1963 (1915); **40**, 174 (1918). Neckers and Kremers, *ibid.*, **50**, 950 (1928).

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PRINCETON UNIVERSITY
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A Mercury Seal for Stirrers

BY D. T. ROGERS

In the past mercury seals for stirrers used in this Laboratory were made from Pyrex glass. They frequently broke because of improper annealing and careless handling.

To overcome these difficulties seals have been made from steel which have proved very satisfactory. The seals made from Allegheny metal No. 22 have remained unattacked after six months of service. Those made from soft steel and covered with a coat of paint have also proved quite satisfactory. The seals weigh about 200 g. and can be used at speeds up to 1000 r. p. m. The upper part of the seal is not shown in the diagram. It consists of either a thin-walled glass or steel cylinder which is fitted to the stirrer shaft with any ordinary rubber stopper. Dimensions are such that stoppers can be changed without dismantling the seals.

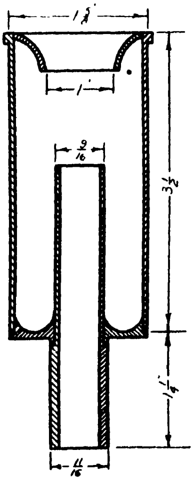

Fig. 1.

The seals were made by A. Bigelman, 1314 Third Avenue, Watervliet, N. Y.

WALKER CHEMICAL LABORATORY
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TROY, NEW YORK

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Pyrolysis of Hydrocarbons. Further Studies on the Butanes[1]

BY CHARLES D. HURD[2] AND FORREST D. PILGRIM[3]

Recent work on the pyrolysis of the butanes[4-10] has elucidated much of the problem but such questions as the following seemed important for further study: (1) the reaction products at incipient decomposition, (2) the importance of the contact time, (3) the relationship of temperature and contact time, (4) the influence of metal reaction tubes. These items, among others, have been considered in the present paper.

The Reaction Products at Incipient Decomposition.—There are two approaches to this problem. One is to extrapolate the quantities of products formed at real conditions to their value at zero decomposition.[8] This method has been considered in the present paper. The other, which will be taken up in the following paper, is to carry out the pyrolysis at a very low decomposition temperature.[10]

The set-up for the pyrolysis experiments was essentially the same as that of Hurd and Spence.[4] The gas was forced through the reaction tube by a head of water. The customary flowmeters, manometer, drying towers and collecting bottles were in the train. Various size reaction tubes and furnaces were used. The gases were analyzed either by the absorption and combustion method[4] or by precision fractional distillation in a column of the type described by Oberfell and Alden[11] and Podbielniak,[12] or by a combination of these methods. The *n*-butane for this work was generously furnished by F. E. Frey of the Phillips Petroleum Company. Distillation analysis confirmed its purity. Less than 1% of low boiling material and less than 1% of higher boiling material was indicated by the Podbielniak type of analysis.[13] Its boiling point was 0°.

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(1) A part of this investigation was financed from funds donated to the American Petroleum Institute by the Universal Oil Products Co. The investigation was listed as Project No. 18.

(2) Director, Project No. 18.

(3) American Petroleum Institute Research Fellow.

(4) Hurd and Spence, THIS JOURNAL, **51**, 3353 (1929).

(5) Pease, *ibid.*, **50**, 1779 (1928); Pease and Durgan, *ibid.*, **52**, 1262 (1930).

(6) Hague and Wheeler, *J. Chem. Soc.*, 378 (1929).

(7) Frolich, Simard and White, *Ind. Eng. Chem.*, **22**, 240 (1930).

(8) Schneider and Frolich, *ibid.*, **23**, 1405 (1931); Neuhaus and Marek, *ibid.*, **24**, 400 (1932).

(9) Frey and Huppke, *ibid.*, **25**, 54 (1933).

(10) Norris and Thomson, THIS JOURNAL, **53**, 3108 (1931); Norris, *J. Chem. Educ.*, **9**, 1890 (1932); Norris and Standley, paper before the Organic Division, A. C. S. meeting at New Orleans, April, 1932

(11) Oberfell and Alden, *Oil Gas J.*, **27**, 142 (1928).

(12) Podbielniak, *ibid.*, **28**, 58 (1929); **29**, 235 (1930).

The extrapolation experiments were essentially similar to those of Neuhaus and Marek so the data will be omitted for brevity. As a primary effect it was confirmed that more propylene than ethylene was formed in the range of 0–30% decomposition and that the dehydrogenation reaction was considerably less than the ethylene reaction. Secondary changes were noticeable in the region of high decomposition for the propylene yield diminished in the 600°-experiments at about 80% decomposition to such an extent that ethylene then predominated. In the 700°-experiments, this occurred in the 60% region.

The Contact Time, VT'/FT''.—(V = vol. of tube; T' = abs. temp. of entering gas: T'' = abs. temp. of heated gas; F = average rate of flow of gas through the tube.)

Experiments were conducted at varying temperatures in tubes of varying sizes and with gas flow of varying rates to ascertain the effect of these factors. As might be expected, no single factor governed the extent of the decomposition but the combination of the various factors, as expressed in the contact time, did do so. The following comparisons make this evident.

New data were obtained with the butanes at 700° in a tube whose heated volume was 5.9 cc. so as to compare them with the published data of Hurd and Spence,[4] who used a tube over ninety times larger, namely, 550 cc. As shown in Table I, contact times of similar magnitude were obtained by maintaining a 75–85 times smaller rate of flow in the smaller tube. The extent of decomposition was comparable and the analysis of the reaction products from the small tube so nearly coincided with the earlier published results with the large tube that, for brevity, it will be omitted here.

TABLE I

FACTORS INFLUENCING THE EXTENT OF DECOMPOSITION

		n-Butane		Isobutane	
Vol. of tube, cc.		5.9	550	5.9	550
Rate of flow, cc./min.	entering	4.45	390	4.7	330
	exit	8.6	740	7.8	595
Final vol. from 1000 cc. of butane		1815	1870	1679	1800
Contact time, sec.		15	18	17	21
Extent of decomposition, %		73	75	77	70

Relationship of Temperature (T) **and Contact Time** (t).—Since $t = VT'/FT''$ it follows that tT'' = constant if V, T' and F are held constant. This inverse relationship between temperature and contact time is in keeping with the fact that the products formed from *n*-butane at about 400° (see the following paper) were similar to those formed at 600 or

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(13) Considerable trouble was experienced with the tanks of the so-called "pure" *n*-butane on the market. For example, on a sample for which 99% purity was claimed, distillation analysis revealed 14.1% propane, 9.1% isobutane and 76.8% *n*-butane.

700° with a shorter contact time. It is apparent also from the data of Table II which show, for example, that at a constant contact time of 0.3 sec. the extent of decomposition may be adjusted at will between 6–95% by selecting a suitable temperature between 650–850°.' Or, with a constant temperature of 600 or 700°, one may govern the extent of decomposition by suitable adjustment of the contact time.

TABLE II

TEMPERATURE, CONTACT TIME AND EXTENT OF DECOMPOSITION

600°				650°		700°				750°		800°		850°	
Sec.	%	C_2H_4	C_3H_6	Sec.	%	Sec.	%	C_2H_4	C_3H_6	Sec.	%	Sec.	%	Sec.	%
0.36	9	..	4.1	0.33	6	0.31	12	4.2	5.5	0.27	24	0.25	70	0.24	95
2.5	24	10.5	11.9			3.7	60	20.0	16.4						
5.2	32	12.7	15.1			4.7	65	19.5	18.7						
24.0	56	18.3	20.1			14.6	73	21.8	15.8						
						20.3	68	15.2	9.8						

The yields of propylene and ethylene from *n*-butane increase with increasing percentage decomposition as the similarity of curve III (propylene yield at 600°) in Fig. 1 with curves I and II (% decomposition at 600 and 700°) bears witness. A curve for ethylene at 600° would be lower than the propylene curve but otherwise similar. Were these two curves plotted for the 700° experiments, the prominence of secondary reactions would be emphasized for the curves would bend downward with increasing contact time.

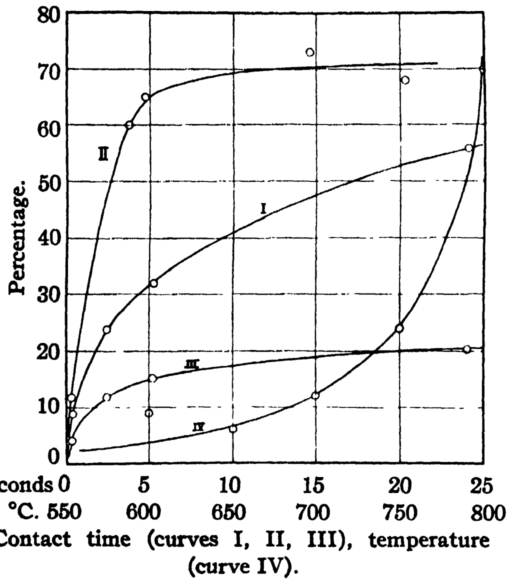

Fig. 1.—Pyrolysis of *n*-butane: curve I, percentage decomposition *vs.* contact time, constant temperature of 600°; curve II, same, for a constant temperature of 700°; curve III, percentage formation of propylene *vs.* contact time, constant temp. of 600°; curve IV, percentage decomposition *vs.* temperature, constant contact time of 0.3 sec.

Curves I, II and III (Fig. 1) are isotherms. Curve IV is not. It represents experiments at a constant contact time of about 0.3 sec., the abscissas representing temperature. The inverse relationship between temperature and contact time is apparent by comparing curves I and IV. If the abscissas (contact time) for curves I, II and III and the ordinates (% decn.) for curve IV are plotted logarithmically, straight line curves are indicated.

The Extent of Decomposition.—Hurd and Spence[4] obtained this value indirectly by averaging the percentage increase in volume with the value of the percentage decomposition (*P*) from the formula $P = (100\ U)/(100 - U)$, wherein *U* represented the percentage of olefins formed. Since *P* may now be determined directly by the Podbielniak type of distillation, some experiments were carried out to compare the two methods. The results in Table III show that the indirect method agrees to within 1–4% for isobutane whereas deviations of 5% or more may be expected with *n*-butane.

TABLE III

DETERMINATION OF UNUSED BUTANE

n-Butane				Isobutane			
Temp., °C.	Contact time, sec.	Decomposition, % I[a]	Decomposition, % D[a]	Temp., °C.	Contact time, sec.	Decomposition, % I[a]	Decomposition, % D[a]
600	5.2	32	37	600	6.2	22.8	22.6
700	2.0	33	29	700	3.8	58.0	62.0
				700	5.1	71.5	70.8

[a] I = Indirect method, calcd. on basis of olefins and increase in volume. D = Direct method, based on combined distillation and absorption analysis.

Pyrolysis Experiments in Metal Tubes.—Three metals were used: iron, nickel and monel. Monel (a Ni–Cu–Fe alloy) was decidedly catalytic. For example, with *n*-butane at 600° and 7.5 seconds the increase in volume was over 200%. The change was largely into carbon and hydrogen. At 500°, however, carbon formation was slight and the reaction appeared to follow a normal course.

TABLE IV

DECOMPOSITION OF THE BUTANES IN METAL TUBES

	n-Butane					Isobutane				
Metal tube	Iron		Ni	Monel		Iron		Ni	Monel	
Temp., °C.	550	600[a]	605	500	600	550	600[a]	600	500	600
Rate of flow, cc./min. entering	131	102	127	183	205	171	117	331	176	268
Rate of flow, cc./min. exit	137	124	151	192	620	184	139	353	190	500
Vol. of heated part of tube, cc.	62	62	121	151	151	62	62	121	151	151
Contact time, sec.	10	9.7	17.8	21	7.5	7.7	9.9	7.2	19.3	8
Final vol. from 1000 cc. butane	1042	1222	1185	1045	3040	1075	1184	1068	1078	1870
Extent of dec., %	14	24	21	20	80	9	19	17	20	70
Analysis of Exit Gases in Per Cent. by Volume										
Isobutylene	..	..	..	..	..	8.7	8.9	4.6	6.8	10.3
Propylene	..	12.0	..	..	..	2.9	6.9	3.7	4.7	7.1
Butenes	..	3.1	..	..	..	..	..	..	..	..
$C_3H_6 + C_4H_8$	11.8	..	12.8	8.9	1.4	..	..	..	..	..
Ethylene	2.4	7.4	5.5	0.9	0.8	0.2	1.2	0.0	0.0	2.5
Hydrogen	..	2.3	4.8	2.6	70.0	1.9	6.7	5.7	5.2	41.5
Methane	..	11.1	..	..	..	2.3	7.5	8.8	..	..
Ethane	..	2.1	..	..	..	..	..	..	..	..
Butane (unused)	..	62.1	..	..	..	84.0	68.9	77.2	..	..
C_nH_{2n+2}	85.8	..	77.0	87.6	28.0	..	..	..	83.3	38.6
n	3.70	..	3.5	3.66	2.40	..	..	..	3.72	2.00

[a] Analysis of the exit gases was by a combination of precision distillation and absorption. For the other runs, analysis was by the absorption method alone.

Iron and nickel tubes differed materially from monel. Pyrolysis in them was practically the same as when Pyrex or quartz tubes were used. Carbonization, which was so prominent in monel at 600°, was negligible in iron or nickel. Representative data are collected in Table IV. If similar experiments in Tables II and IV are compared the essential similarity of results in the quartz, nickel and iron tubes is apparent.

In another article[14] it will be shown that iron and nickel tubes exert a considerable catalytic influence (dehydrogenation and carbonization) on the decomposition of such unsaturated hydrocarbons as ethylene, propylene, isobutylene and 2-pentene. This shows that the effect is governed not only by the nature of the metal but also by the type of hydrocarbon.

Seamless nickel, iron and monel tubes were used in this investigation. The iron tube was calorized on the outside (but not on the inside). The thermocouple within each tube was encased by a Pyrex sheath. The metal tubes were encased at the furnace limits with tight-fitting copper coils through which cold water circulated. This permitted the use of rubber connections at the ends of the tubes. After each run the tubes were searched for carbon and scraped clean if any was present. The monel tube produced much carbon but almost none was formed in the nickel and iron tubes. For example, in the 600° runs with *n*- and isobutane in monel, 15 and 46%, respectively, of the carbon content of the entering gas was scraped from the walls of the tube as carbon.

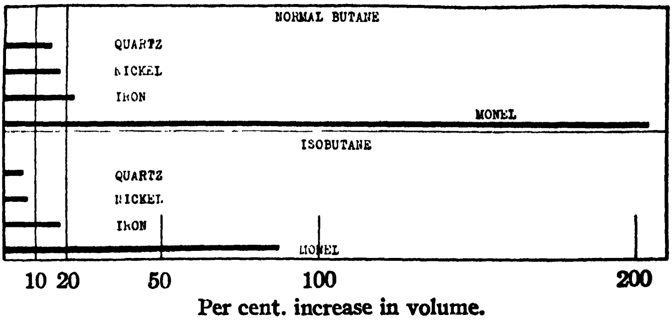

Fig. 2.—Relative catalytic effect of various tubes.

The percentage increase in volume in the 600°-experiments was calculated from the data (listed as "final vol. from 1000 cc. butane") in Table IV and the results portrayed graphically in Fig. 2. Although the contact times vary somewhat, the striking behavior in monel is evident.

Search for Isobutylene in the Products from *n*-Butane.—In the absorption method of analysis for hydrocarbons, isobutylene is removed by 62.5% sulfuric acid. Slight absorption in this reagent was noticed when the gases from pure *n*-butane pyrolyses were analyzed. Using a solution of

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(14) With L. K. Eilers.

nitric acid and mercuric nitrate which was shown by Denigès[15] to be a specific reagent for isobutylene, Mr. A. R. Goldsby demonstrated the absence of isobutylene in these gases. Hence, the slight absorption in the 62.5% acid was an absorption either of propylene or of butane which was present in large amounts. Thus, it is obvious that the absorption method, which is quite satisfactory for isobutylene when appreciable quantities are present, must be used with caution when only traces are present.

The test reagent for isobutylene was prepared by dissolving 20 g. of mercuric oxide in 40 cc. of concd. nitric acid and 500 cc. of water. It was found that 300 cc. of the reagent absorbed 150 cc. of pure 1-butene gas readily enough but there resulted no precipitate even on standing overnight. Similarly, there was absorption but no consequent precipitation when 2-butene or trimethylethylene was taken. With isobutylene, however, a distinct precipitation (yellow) was observed in two hours with a 0.1-cc. sample. A similar orange colored precipitate was produced in a few minutes if the solution was heated.

A sample of butane, pyrolyzed at 675° and twenty-three seconds contact time, was analyzed as follows: 1.7% absorbed by 62.5% acid and usually interpreted as isobutylene, 22.8% propylene, 19.2% ethylene, 5.3% hydrogen, 51% saturated hydrocarbons. When this gaseous mixture was tested with the acidified mercuric nitrate reagent no trace of precipitation occurred. Hence, no isobutylene was formed during the pyrolysis.

Summary

Experiments with the butanes have demonstrated that similar results may be expected in tubes of widely varying sizes if a constant contact time is maintained in the various tubes. The inverse relationship between temperature and contact time is pointed out.

Decomposition of *n*- or isobutane in iron or nickel tubes at 600° pursued practically the same course as that observed in quartz tubes. Monel, however, exerted a vigorous catalytic action at this temperature. The change was largely one into carbon and hydrogen.

The fact that no isobutylene was formed during the pyrolysis of *n*-butane is sufficient evidence that the carbon chain does not undergo rearrangement in this process.

EVANSTON, ILLINOIS

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[15] Denigès, *Compt. rend.*, **126**, 1043 (1898).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND STANFORD UNIVERSITY]

The Preparation of Crotylmagnesium Bromide. The Effect of Solvents on the Yield of Crotyl and Allylmagnesium Bromides[1]

BY WILLIAM G. YOUNG, ARTHUR N. PRATER AND SAUL WINSTEIN

In a previous communication[2] the authors reported the formation of mixtures of crotyl and vinylmethyl carbinyl bromides during the preparation of butene from *trans* crotonaldehyde. The most promising method of studying these allylic mixtures of bromides is to convert them into the Grignard reagent, since this reagent may be quickly decomposed to form butene mixtures which may be analyzed.[3] In view of the importance of the Grignard reagent for this purpose we are presenting in this paper an account of the preparation of crotylmagnesium bromide in diethyl and dibutyl ethers.

Crotylmagnesium bromide heretofore has never been isolated as a distinct preparation. Braun and Shermacker[4] have reported that this reagent couples with additional crotyl bromide to give 2,6-octadiene almost exclusively. This coupling phenomenon is common with allyl halides and with β substituted allyl halides. It is only recently that Gilman and coworkers have successfully prepared Grignard reagents from this type of compounds.[5] Like other β substituted allyl halides, crotyl bromide requires special conditions in order to obtain maximum yields of the Grignard reagent. Although these conditions are different for each solvent it is possible to obtain excellent yields of crotylmagnesium bromide[6] in both diethyl and dibutyl ethers.

Experimental Procedure

The Preparation of Crotyl Alcohol.—Crotyl alcohol, b. p. 117–119°, was obtained from the reduction of crotonaldehyde with zinc and acetic acid, with magnesium chloroethylate or with platinum catalyst and hydrogen. It always contained some butyl alcohol, 5–50%, which could not be removed by distillation. Since any attempt to separate crotyl and butyl alcohols might bring about molecular rearrangements, the mixtures were carried through the Grignard stage without previous separation. At this stage the undesirable butyl constituent was eliminated as butane. Consequently, the alcohol mixtures were analyzed for crotyl content by titration with bromine before being used.

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[1] Preliminary experiments on this investigation were performed by the senior author while serving as a National Research Council Fellow in Chemistry at Stanford University and were continued at the University of California at Los Angeles. This paper was presented at the Pasadena meeting of the American Association for the Advancement of Science, June 19, 1931.

[2] Young and Prater, THIS JOURNAL, 54, 404 (1932).

[3] Dillon, Young and Lucas, *ibid.*, 52, 1953 (1930).

[4] Braun and Shermacker, *Ber.*, 56, 538 (1922).

[5] (a) Gilman and McGlumphy, *Bull. soc. chim.*, 43, 1322 (1928); (b) Gilman and Kirby, THIS JOURNAL, 51, 3475 (1929); (c) Gilman and Zoellner, *ibid.*, 52, 3984 (1930); (d) Gilman and Harris, *Rec. trav. chim.*, 50, 1052 (1931).

[6] Although we are obviously working with crotyl bromide containing some vinyl methyl carbinyl bromide the expressions "crotyl bromide" and "crotylmagnesium bromide" are used for simplicity throughout this paper.

Preparation of Crotyl Bromide.[6]—Crotyl bromide contaminated with butyl bromide was prepared from mixtures of crotyl and butyl alcohols by the action of phosphorus tribromide in pyridine, according to the procedure of Kirrmann as modified by Prévost.[7] The boiling range of the product varied from 4–10° depending on the amount of butyl bromide present. The crotyl bromide content of the product was assumed to be the same as the crotyl alcohol content of the original alcohol mixtures. The assumed compositions were later verified by the slow addition of bromine to the bromide mixtures over a period of forty-eight to sixty hours (see Table I for the composition of these mixtures). The crotyl bromide used for the experiments listed in Table II was prepared, free from butyl bromide, by the action of hydrobromic acid, saturated at 0°, on mixtures of crotyl and butyl alcohols according to Charon's method.[8]

Purification of Solvents.—Two sources of dibutyl ether were used: Eastman product, b. p. 141–142°, and a product prepared in this Laboratory. The ether was refluxed with acidified potassium permanganate, washed with water and sodium bicarbonate and dried with calcium chloride. Before it was distilled it was refluxed with molten sodium for several hours to remove the last traces of butyl alcohol; b. p. 142°.

Dry diethyl ether was prepared in the customary manner.

Preparation of Crotylmagnesium Bromide.[6]—The crotylmagnesium bromide was prepared in a nitrogen-filled dry flask which was fitted with a dropping funnel, a mercury-sealed mechanical stirrer, and an upright spiral condenser which was protected with a phosphorus pentoxide tube. The magnesium turnings were *vigorously* stirred with sufficient ether, ethyl or butyl, to cover them while an ether solution of crotyl bromide was added dropwise over a period of two to four hours. In the experiments listed in Table II, where the crotyl bromide[8] was free from butyl bromide, the yield of RMgX was determined by titration of aliquot portions of the ether solution.[9] However, if mixtures of crotyl and butyl bromides were used the solvent was removed at reduced pressures and the RMgX mixture was decomposed with 2 normal sulfuric acid. The resulting mixtures of butane and butene were passed through a purification train of 23% perchloric acid, soda lime and calcium chloride, and into a bromination flask where the butene was trapped as dibromobutane. The yield of crotylmagnesium bromide was based on the weight of dibromobutane obtained after the latter had been washed, dried and distilled. In order to locate the cause for low yields in the early experiments some of the Grignard reagents were treated with dilute nitric acid and analyzed for bromide ion (see experiments 3 and 4, Table II). The results proved that sufficient time had been allowed for all of the crotyl bromide to react to form either crotylmagnesium bromide or 2,6-octadiene. The lower yield of RMgX was due to interference by the coupling reaction and not to incomplete reaction of the crotyl bromide.

Discussion of Results

Diethyl Ether in the Preparation of Crotylmagnesium Bromide.[6]—The experiments on the preparation of crotylmagnesium bromide in diethyl ether are listed in Table I. It is evident from experiments 1–4 that crotyl bromide exhibits a greater tendency to couple with the Grignard reagent than does allyl bromide, thus leading to smaller percentage yields of RMgX under the same conditions. However, the yield of crotylmagnesium bro-

(7) (a) Kirrmann, *Bull. soc. chim.*, [4] **39**, 698 (1926); (b) Prévost, *Ann. chim.*, [10] **10**, 147–81 (1928).

(8) Charon, *Ann. chim. phys.*, [7] **17**, 233 (1897).

(9) See Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

mide may be improved rapidly by increasing the time of addition of the bromide and the ratio of solvent to bromide, as well as using 20–30 mesh magnesium turnings which are prepared just before use (see experiments 6–8). Magnesium–copper alloy has a detrimental effect on the yield of the Grignard reagent just as it does with allylmagnesium bromide.[10]

TABLE I

CROTYLMAGNESIUM BROMIDE[6] IN DIETHYL ETHER[e]

Expt.	Crotyl bromide in mixture, %	Moles of crotyl bromide[6]	Mole ratio Solvent Bromide	Mole ratio Mg Bromide	Time for bromide addition, min.	Yield of RMgX, %	Notes
1	50	0.10	7.5	3.0[b]	200	27.7[a]	
2		0.374	7.5	3.0[c]	95	72.5	Duplicate of Gilman's experiments using allyl bromide in place of crotyl bromide
3		0.200	7.5	3.0[c]	205	90.0	
4	70	0.374	7.5	3.0[c]	205	55.0	Duplicate of 3 using crotyl bromide
5	50	0.20	7.5	3.0[d]	205	3.0	
6	50	0.40	8.5	3.0[c]	275	80.0	
7	63	0.40	9.5	3.0[c]	275	91.0	
8	99.5	0.20	9.5	3.0[c]	275	90.0	Duplicate of 7 using pure crotyl bromide

[a] The same procedure as recommended by Gilman for allylmagnesium bromide. [b] Commercial magnesium turnings. [c] 20–30 mesh magnesium turnings prepared just before use from a bar 99.5% pure. [d] Magnesium–copper alloy: 88% Mg–12% copper. [e] Duplicate or triplicate runs of experiments 4–8 agreed within 2%.

TABLE II

CROTYL[6] AND ALLYLMAGNESIUM BROMIDE IN DIBUTYL ETHER[e]

Expt.	Moles of bromide	Mole ratio Solvent Bromide	Mole ratio Magnesium Bromide	Time for bromide addition, min.	Yield of RMgX, %	Notes
1	0.08[c]	6.1[d]	3.0	175	34.0	
2	.10[c]	9.5	3.0	180	45.0	
3	.10[c]	19.0	3.0	180	52.0	Total Br⁻ = 101% Medium stirring
4	.05[c]	38.0	6.3	180	62.0	Total Br⁻ = 100.2% Medium stirring
5	.035[c]	76.0	9.2	205	73.0	Medium stirring
6	.05[c]	38.0	6.3	180	77.0	Rapid stirring
7	.03[c]	76.0	11.0	157	95.7	Rapid stirring
8	.03[c]	76.0	12.0	170	100.2	Excellent stirring
9	.20[a]	4.7[b]	3.0	75	56.0	
10	.10[a]	9.5	3.0	190	77.5	
11	.05[a]	19.0	6.0	165	83.0	Rapid stirring
12	.05[a]	38.0	6.0	170	82.0	Medium stirring
13	.035[a]	38.0	12.0	180	99.0	Excellent stirring

[a] Allyl bromide. [b] This mole-ratio gives the same concentration in moles of bromide per cc. of solvent as the 7.5 mole ratio in diethyl ether. Compare yield with Experiment 3, Table I. [c] Crotyl bromide[6] (99.5% unsaturation). [d] This mole ratio gives the same concentration in moles of bromide per cc. of solvent as the 9.5 mole ratio in diethyl ether. Compare experiments 7 and 8, Table I. [e] Duplicate runs agreed within 2–5% when the rate of stirring was accurately controlled.

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[10] Johnson and Adkins, This Journal, 53, 1520 (1931); 54, 1943 (1932).

Dibutyl Ether as a Solvent for Preparing Unsaturated Alkylmagnesium Bromides.—In studying the decomposition of crotylmagnesium bromides prepared from crotyl bromides having different sources, we were unable to prevent traces of diethyl ether from being carried over with the hydrolysis products. As a result dibutyl ether was investigated as a solvent since it is less volatile and has been used effectively to replace diethyl ether for preparing saturated alkylmagnesium halides.[11] It was found that the yield of RMgX was greatly affected by this change in solvents. We therefore determined the optimum conditions for obtaining maximum yields of RMgX using allyl bromide before proceeding with crotyl bromide, which is difficult to prepare in quantity. The results from both bromides are listed in Table II. The tendency to coupling is far more pronounced in dibutyl than in diethyl ether, especially with crotyl bromide. It is necessary to use much larger ratios of solvent and of magnesium to bromide in order to obtain yields of RMgX which correspond to those with diethyl ether. Extremely vigorous stirring is necessary when using butyl ether. The advantage gained by using an increased ratio of solvent to bromide will be lost if the magnesium is not kept in intimate contact with all parts of the solution during the entire run (compare experiments 4 and 5 with 3, 6, 7, 8, and 12 with 11 and 13).

The authors are indebted to Doctors G. Ross Robertson and Francis E. Blacet for their kindly interest in this work.

Summary

Crotylmagnesium bromide has been isolated for the first time. The use of the reagent in the study of mixtures of crotyl and vinyl methyl carbinyl bromides is discussed. Optimum conditions are reported for obtaining excellent yields of crotylmagnesium bromide in both diethyl and dibutyl ethers. The effect of solvent on the yields of both crotyl and allylmagnesium bromides is discussed.

LOS ANGELES, CALIFORNIA

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[11] Marvel, Blomquist and Vaughn, THIS JOURNAL, 50, 2810 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Some Ammonolytic Reactions[1]

BY EDWARD C. FRANKLIN

Ammono Carbonic Acid Esters. Esters of Cyanamide.—It has been shown that cyanamide is an ammono carbonic acid, which is to say that it is a derivative of ammonia in the same sense that ordinary carbonic acid may be said to be a derivative of water.[2] Such being the case it follows that the alkyl and aryl derivatives of cyamamide are to be regarded as ammono carbonic acid esters.

The methods for the preparation of diethylcyanamide, for example, and its behavior toward hydrolyzing agents are in accordance with the assumption that it is a diethyl ammonocarbonate. It has been prepared by the action of disodium cyanamide on ethyl iodide, $C_2H_5I + Na_2NCN = (C_2H_5)_2NCN + 2NaI$, by the interaction of cyanogen bromide, a carbonic acid bromide, and diethylamine, $NCBr + (C_2H_5)_2NH = (C_2H_5)_2NCN + HBr$, and is hydrolyzed by the action of aqueous hydrochloric acid to diethylamine, carbon dioxide and ammonia, $(C_2H_5)_2NCN + H_2O = (C_2H_5)_2NH + HOCN \xrightarrow{+H_2O} CO_2 + NH_3$. Looked upon as an ammono carbonic acid ester diethylcyanamide should undergo ammonolytic decomposition under the action of potassium amide in liquid ammonia solution by the equation $(C_2H_5)_2NCN + 2KNH_2 = (C_2H_5)_2NH + K_2NCN + NH_3$, which represents a reaction closely analogous to the hydrolytic reaction involved in the conversion of ethyl aquocarbonate into aquo ethyl alcohol and potassium aquocarbonate under the action of aqueous potassium hydroxide, $OC(OC_2H_5)_2 + 2KOH = K_2CO_3 + 2C_2H_5OH$.

Accordingly Griswold accomplished the ammonolysis of the following esters of cyanamide by warming them, at 35°, in liquid ammonia solution with potassium amide. The percentage yields of the ammonolytic products are given under K_2CN_2 and R_2NH.

Ester	Formula	K_2CN_2		R_2NH		
Diethylcyanamide	$(C_2H_5)_2NCN$	100		64	72	75
Di-*n*-propylcyanamide	$(C_3H_7)_2NCN$	99	98	86	78	
Diisobutylcyanamide	$(C_4H_9)_2NCN$	101	100	75	67	

Since dipotassium cyanamide is insoluble in liquid ammonia, its quantitative separation from the reaction mixture was easily accomplished. The quantitative recovery of the soluble amines from a large excess of ammonia is not a simple matter.

Esters of Guanidine.—The alkyl and aryl derivatives of guanidine, like those of cyanamide, are ammono carbonic acid esters and as such

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(1) The laboratory work upon which this report is based was done by Christian W. Niemann, Thesis, Stanford University, 1926, Gale G. Griswold, Thesis, Stanford University, 1926, and by Faw Yap Chuck.

(2) Franklin, THIS JOURNAL, 44, 490 (1922).

should be susceptible to ammonolytic decomposition in a manner resembling the hydrolytic decomposition of the aquocarbonates. But one such compound has been studied in respect to its ammonolytic behavior in liquid ammonia solution.

N,N′,N″-Triphenylguanidine, $C_6H_5N{=}C(NHC_6H_5)_2$.—Beyond the formation of a dipotassium salt[3] potassium amide is without action on triphenylguanidine even when the solution is heated. When, however, the ester is heated at 200° in liquid ammonia solution with hydrochloric acid (ammonium chloride), it is ammonolyzed to guanidine and aniline as represented by the equation

$$C_6H_5N{=}C(NHC_6H_5)_2 + 3NH_3 = HN{=}C(NH_2)_2 + 3C_6H_5NH_2$$

A typical experiment gave 82% of the calculated amount of aniline based on the preceding equation, and an abundant yield of guanidine isolated in the form of its picrate. N,N′,N″-Triphenylguanidine, it may be recalled, is hydrolyzed by the action of aqueous hydrochloric acid at 250° to aniline, carbon dioxide and ammonia.

Metallic Salts of Acid Guanidine Esters.—Several metallic salts of N,N′,N″-triphenylguanidine, which is an acid ester of an ammono carbonic acid, have been prepared.[3]

When potassium amide and dialkylcyanamides are brought together in cold liquid ammonia solution, products are formed as represented by the equation $R_2NCN + KNH_2 = R_2NC(NH)NHK$. The following named and formulated potassium salts of dialkylguanidines have been prepared.

		Analyses, %			
		Metal		Nitrogen	
Ester-salt	Formula	Calcd.	Found	Calcd.	Found
K-Dimethylguanidine	$(CH_3)_2NC(NH)NHK$	31.2	31.6	33.6	34.4
			31.5		34.0
K-Diethylguanidine	$(C_2H_5)_2NC(NH)NHK$	25.5	25.6	27.4	27.0
			25.2		27.2
K-Diisopropylguanidine	$(C_3H_7)_2NC(NH)NHK$	21.5	21.5	23.2	23.1
			21.4		23.3
			21.2		
K-Diisobutylguanidine	$(C_4H_9)_2NC(NH)NHK$	18.7	18.4	20.1	20.1
			18.9		19.4
			18.6		20.0
K-Diisoamylguanidine	$(C_5H_{11})_2NC(NH)NHK$	16.5	16.1	17.7	18.0
			16.7		17 8
Na-Diethylguanidine	$(C_2H_5)_2NC(NH)NHNa$	16.4	16.2	30.0	30.5
			16.5		30.3
Na-Diisobutylguanidine	$(C_4H_9)_2NC(NH)NHNa$	11.9	11.6	21.8	21.3
			12.0		21.4

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[3] Franklin, THIS JOURNAL, **44**, 490 (1922).

Unfortunately nothing is known concerning these compounds beyond the facts that they are formed by the direct addition of the alkali metal amides to the respective dialkylcyanamides, that they have been obtained well crystallized and of sharply definite composition and that they are fairly soluble in liquid ammonia. Circumstances brought an end to Griswold's work before he had determined definitely whether or not these compounds are derivatives of guanidine. That they are, however, is highly probable.

Aquo-Ammono-Carbonic Acid Esters.—Urea is an aquo-ammono carbonic acid of which O-esters and N-esters are known. The ammonolytic behavior of two urea esters has been observed.

N-Methylurea, $H_2NCONHCH_3$.—Methylamine, urea and guanidine have been identified as products of the ammonolytic decomposition of methylurea.

N,N′-Diphenylurea, $OC(NHC_6H_5)_2$.—In accordance with the equation $OC(NHC_6H_5)_2 + 2NH_3 = OC(NH_2)_2 + 2C_6H_5NH_2$, Niemann[4] obtained a 77% yield of aniline together with undetermined amounts of urea when he heated this phenyl aquo-ammono-carbonate in liquid ammonia solution with ammonium chloride. Guanidine was formed at the same time as the result of the ammonolysis of a portion of the urea formed.[5] Ammonia in alcoholic solution at 150° ammonolyzes diphenylurea to aniline and urea. Under the action of aqueous hydrochloric acid the ester is hydrolyzed to aniline, carbon dioxide and ammonia.

Carbazylic Acid Esters and Carboxazylic Acid Esters.—As is well known ammonium acetate when heated is partly converted into acetamide. An aquo acetic acid is thereby ammonolyzed to an aquo-ammono acetic acid. Chuck found that when either ammonium acetate or acetamide is heated in liquid ammonia solution with ammonium chloride, liberal yields of acetamidine are formed. Inversely, acetamidine, which is an ammono acetic acid, is readily hydrolyzed first to acetamide and thence to acetic acid. The reversible reactions involved are represented by the equation

$$CH_3COOH \xrightarrow[-H_2O]{+NH_3} CH_3CONH_2 \xrightarrow[-H_2O]{+NH_3} CH_3C(NH)NH_2.$$

Niemann found that diphenylacetamidine and diphenylbenzamidine, when heated with ammonium chloride in liquid ammonia solution, are ammonolyzed, the one to acetamidine and aniline, $CH_3C(NC_6H_5)NHC_6H_5 + 2NH_3 = CH_3C(NH)NH_2 + 2C_6H_5NH_2$, the other to benzamidine and aniline, and that acetanilide under similar treatment gives abundant yields of acetamidine and aniline. That acetamidine was obtained instead of acetamide is accounted for by the above-noted observation by Chuck to the effect that acetamide is ammonolyzed to acetamidine under the condi-

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(4) Niemann, Thesis, Stanford University, 1926.

(5) Blair, THIS JOURNAL, 48, 87 (1926).

tion of Niemann's experiments. By the action of dilute aqueous acids or alkalies, acetanilide is hydrolyzed to aquo acetic acid and aniline.

Acid Chlorides.—Benzotrichloride, $C_6H_5COCl_3$, is hydrolyzed by the action of water at 150° to aquo benzoic acid. It is simultaneously hydrolyzed and ammonolyzed by the action of aqua ammonia at 130° to aquo benzoic acid, aquo-ammono-benzoic acid (benzamide) and benzoic anammonide (benzonitrile). Niemann obtained a 75% yield of benzonitrile by allowing a liquid ammonia solution of benzotrichloride to stand at laboratory temperatures for some time. When he heated such a solution for a time at 100°, good yields of monomolecular and trimolecular benzonitrile were obtained.

Summary

An account is given of the ammonolytic behavior of three dialkylcyanamides, of triphenylguanidine, of two N-esters of urea, of acetic acid and acetamide, of diphenylacetamidine and diphenylbenzamidine, of acetanilide and of benzotrichloride.

It is shown that the dialkylcyanamides unite with alkali metal amides at low temperatures in liquid ammonia solution to form metallic salts of dialkylguanidines.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Metallic Salts of Carboxazylic Acids[1]

BY EDWARD C. FRANKLIN

In this Laboratory we have come to use the general name carbylic acids to include the closely related carboxylic acids, the acid amidines and the acid amides and to speak of the three classes of compounds as carboxylic acids, carbazylic acids and carboxyazylic acids, respectively. Acetic acid, acetamidine and acetamide are examples of the three classes of compounds. Acetic acid and acetamidine we regard as acetic acids belonging, respectively, to an oxygen system and a nitrogen system of compounds.[2] The first acid, as a derivative of water, is an aquo acetic acid, the second, as a derivative of ammonia, is an ammono acetic acid, while acetamide, which may be said to be derived at the same time from water and ammonia, is an aquo-ammono acetic acid.

In many ways the acid amidines and the acid amides closely resemble the carboxylic acids. For example, Franklin and Stafford[3] showed that

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(1) The laboratory work upon which this report is based was done by Ruth V. Fulton, Thesis Stanford University, 1925.

(2) Franklin, *Am. Chem. J.*, **47**, 285 (1912); Fernelius and Johnson, *J. Chem. Educ.*, **5**, 664, 828 (1928); **7**, 1291, 1602, 1850 (1930).

(3) Franklin and Stafford, *Am. Chem. J.*, **28**, 83 (1902).

certain acid amides in liquid ammonia solution react with the alkali metals and their amides and with metallic magnesium to form salts strictly after the manner of the formation of metallic salts by the action of carboxylic acids in water solution, and Cornell[4] found that metallic salts of the acid amidines may be prepared by using liquid ammonia in which to carry out the necessary reactions.

This paper is written to place on record the preparation of a number of metallic salts of carboxyazylic acids and to give the results of their pyrogenetic decomposition as observed by Miss Fulton. The general methods of manipulation used in preparing these salts are described elsewhere.[5]

The salts listed were obtained by the action of alkali metal amides on the respective acid amides in liquid ammonia solution.

SALTS OF CARBOXAZYLIC ACIDS

		Analyses, %							
		Metal				Nitrogen			
Salt	Formula	Calcd.	Found			Calcd.	Found		
K-Formate	HCONHK	47.0	46.6	46.9	46.8	16.8	16.1	16.2	16.9
Na-Formate	HCONHNa	34.3	34.4			20.9	21.1		
K-Propionate	C_2H_5CONHK	35.2	35.5			12.6	12.1		
K-Isobutyrate	C_3H_7CONHK	31.2	30.8			11.2	11.8		
K-Valerate	C_4H_9CONHK	28.0	27.7	27.2	27.2	10.0	10.0		
K-Caproate	$C_5H_{11}CONHK$	25.5	25.2	24.7		9.1	8.5	9.0	
K-Benzoate	C_6H_5CONHK	25.6	25.6			8.8	8.8		
K-Palmitate	$C_{15}H_{31}CONHK$	13.2	12.8			4.8	4.5		
K-Malonamide	$CHK(CONHK)_2$	54.1	54.8	53.7		13.8	13.5	13.4	12.9

All these salts, excepting potassium palmitamide and tripotassium malonamide which are formed as amorphous precipitates when dilute solutions of the respective acid amides are added to an excess of potassium amide in dilute solution, are soluble in liquid ammonia and were obtained well crystallized. They are all vigorously hydrolyzed by the action of water to the respective alkali metal hydroxides and acid amides.

Pyrogenetic Decomposition of the Potassium Carboxazylates.—Just as the alkali metal carboxylates when heated with soda-lime yield saturated hydrocarbons and alkali metal aquocarbonates, sodium acetate for example in accordance with the equation, $CH_3COONa + NaOH = CH_4 + Na_2CO_3$, and as potassium ammonoacetate, when heated with potassium amide, forms methane and a potassium ammonocarbonate, $CH_3C(NH)NHK + KNH_2 = CH_4 + K_2CN_2$,[4] so, at elevated temperatures, the potassium salts of the acid amides might be expected to decompose in accordance with the equation $RCONHK = RH + KNCO$, to form saturated hydrocarbons and a potassium aquo-ammono-carbonate. As a matter of fact that is what happens except that a portion of the salt simul-

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(4) Cornell, THIS JOURNAL, **50**, 3311 (1928).

(5) Franklin, *ibid.*, **27**, 820 (1905); *J. Phys. Chem.*, **15**, 509 (1911); THIS JOURNAL, **35**, 1453 (1913).

taneously decomposes into a nitrile and potassium hydroxide, $RCONHK = RCN + KOH$.

In accordance with the scheme, $RCONHK \begin{matrix} \nearrow RH + OCNK \\ \searrow RCN + KOH \end{matrix}$, Miss Fulton found that at temperatures around 250–300° four potassium carboxylates decomposed to yield potassium cyanate and potassium hydroxide in the following molecular ratios; potassium propionamide 33/67, potassium isobutyramide 25/75, potassium valeramide 38/72, potassium capronamide 28/72. At the same time the first salt was found to yield ethane and propionitrile, the second, propane and butyronitrile, the third, normal butane and valeronitrile, the fourth, normal pentane and capronitrile. Neither benzonitrile nor potassium hydroxide was found among the decomposition products of potassium benzamide. Approximately quantitative yields of benzene were obtained. Excepting in the case of the latter salt considerable amounts of dark colored, amorphous residues were formed. Potassium cyanate in liberal quantities, potassium hydroxide in small amounts, and a high boiling liquid which was assumed to be a mixture of pentadecane and palmitic acid nitrile were found among the decomposition products of potassium palmitamide.

Summary

Alkali metal salts of nine acid amides (carboxazylic acids) have been prepared by the action of alkali metal amides on the respective acid amides in liquid ammonia solution.

When heated in the dry state these salts yield saturated hydrocarbons and potassium cyanate (potassium aquo-ammono-carbonate).

Attention is called to the close resemblance between the reactions represented by the equations, (1) $RCOOK + KOH = RH + K_2CO_3$, (2) $RC(NH)NHK + KNH_2 = RH + K_2CN_2$ and (3) $RCONHK = RH + KNCO$.

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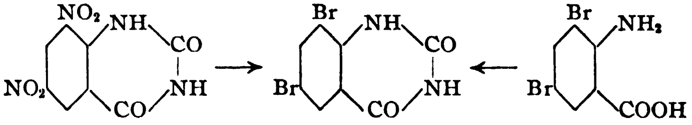
6,8-Dibromobenzoylene Urea and the Constitution of Dinitrobenzoylene Urea

BY F. E. SHEIBLEY AND D. P. TURNER

By the direct nitration of benzolyene urea in sulfuric acid solution Bogert and Scatchard obtained a dinitro derivative which exhibited a sharp color change when used in acidimetric titrations. They investigated the limits of this change and dinitrobenzoylene urea has since assumed some importance as an indicator.[1] In a later paper the same authors[2] describe the preparation of 6-nitrobenzoylene urea by nitration with the theoretical amount of nitric acid. This compound was identified through its formation from methyl 2-nitrouramino-5-nitrobenzoate by the action of ammonia, and on further nitration was easily converted into dinitrobenzoylene urea. From the ease with which it is introduced they considered the most probable location of this second entering nitro group to be the 8-position, and an experimental verification of this conclusion is now realized.



I II III

6,8-Dinitrobenzoylene urea (I) was reduced and the resulting diamine[3] completely diazotized, the double diazonium salt thus obtained being converted into 6,8-dibromobenzoylene urea (II) by means of a Sandmeyer reaction. 3,5-Dibromoanthranilic acid (III) was fused with urea and the melt extracted with low-boiling solvents, leaving a residue of 6,8-dibromobenzoylene urea (II) identical with the corresponding substance (II) prepared from dinitrobenzoylene urea (I). Attempts to form the intermediate 3,5-dibromo-2-uraminobenzoic acid by treating acidic solutions of (III) in various solvents with potassium isocyanate were unsuccessful, the dibromoanthranilic acid being recovered unchanged. 5-Bromoanthranilic acid, however, is known to react with isocyanic acid under similar conditions to form the corresponding uramino acid, which can be easily dehydrated[4] to give the alkali-soluble 6-bromobenzoylene urea. The latter compound is now obtained by fusing 5-bromoanthranilic acid with urea. Conversely, and in agreement with the experience of Bogert and Scatchard with 5-nitroanthranilic acid,[5] 3,5-dinitroanthranilic acid was unaffected by fusion with urea, the similarity of the properties of the acid

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(1) Bogert and Scatchard, THIS JOURNAL, **38**, 1606 (1916).

(2) Bogert and Scatchard, *ibid.*, **41**, 2052 (1919).

(3) Ref. 2, p. 2060.

(4) Scott and Cohen, *J. Chem. Soc.*, **123**, 3187 (1923).

(5) Ref. 2, pp. 2053 and 2054.

with those of the product sought rendering improbable the detection of any small amounts of (I) that may have been formed. Other experiments designed to condense urea with 3,5-dinitro-2-chlorobenzoic acid resulted only in the formation of 3,5-dinitroanthranilic acid.

6,8-Dibromobenzoylene urea (II) is a high-melting, inert substance, soluble only in high-boiling solvents. Solutions of sodium and potassium hydroxides fail to dissolve it appreciably due to the formation of sparingly soluble salts. With the hydroxides of the other alkali metals, however, it is more soluble, forming solutions which yield a precipitate of the sodium salt directly when treated with aqueous solutions of sodium salts. The corresponding potassium salt may likewise be precipitated, but the separation is slower and less complete, and requires the use of stronger solutions than is the case with the sodium compound. From a series of comparative precipitation tests the order of increasing solubility of the alkali-metal salts of 6,8-dibromobenzoylene urea is found to be: Na, K, Li, Rb, Cs.

Unlike 6,8-dinitrobenzoylene urea, which could not be alkylated,[6] 6,8-dibromobenzoylene urea reacts with alkylating agents to form alkali-soluble monoalkyl derivatives. Of these, 3-ethyl-6,8-dibromobenzoylene urea possesses the more convenient properties and was studied, the ethyl group being assigned to the 3-position by analogy with previous observations[7] on the alkylation of benzoylene urea.

These experiments were performed in the laboratory of Dr. N. A. Lange, to whom the authors are indebted.

Experimental Part

Preparation of 6,8-Dibromobenzoylene Urea (II) from 6,8-Dinitrobenzoylene Urea (I).—6,8-Dinitrobenzoylene urea was reduced to the corresponding diamine by means of stannous chloride and concentrated hydrochloric acid, and the hydrochloride thus formed converted into the free base through treatment with ammonia.[3] A suspension of the free base, 6,8-diaminobenzoylene urea, in 30% hydrobromic acid was boiled for a few minutes, allowed to cool, and the insoluble hydrobromide removed by filtration and dried.

To 25 cc. of 30% hydrobromic acid diluted with 125 g. of ice and cooled externally with an ice and salt mixture, was added a cold aqueous solution of 3.75 g. of sodium nitrite. The resulting mixture was then stirred mechanically while 4.3 g. of 6,8-diaminobenzoylene urea hydrobromide suspended in 25 cc. of 30% hydrobromic acid was added slowly. By continuing the stirring and cooling for an hour a clear yellow solution was obtained. Attempts to diazotize the diamino compound by adding sodium nitrite to it in acid solution resulted in the formation of dark red precipitates.

A one liter, three-necked flask was equipped with a water-cooled reflux condenser, a thistle tube and a steam inlet tube both reaching to the bottom of the flask, and a thermometer the bulb of which was immersed in the reaction mixture; following, in general, the directions given elsewhere[8] for effecting a Sandmeyer reaction by the so-called hot method. Two grams of cuprous bromide was added to 80 cc. of 30% hydro-

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(6) Ref. 2, p. 2053.

(7) Lange and Sheibley, THIS JOURNAL, 55, 2113 (1933).

(8) Fry and Grote, *ibid.*, 48, 710 (1926).

bromic acid in the flask which was then warmed with a flame and steam passed in until the temperature reached 100°, when the solution of the diazonium salt prepared as described above was slowly introduced through the thistle tube, the temperature being maintained at 100–105°. A vigorous evolution of gas occurred and a pale brown precipitate separated. The mixture was heated and stirred with steam for ten minutes following the addition of all of the diazonium salt, and was then allowed to cool to 70°, after which the 2.1 g. of precipitated 6,8-dibromobenzoylene urea was removed by filtration, washed with water, and dried, m. p. 297°.

Preparation of 6,8-Dibromobenzoylene Urea (II) from 3,5-Dibromoanthranilic Acid (III).—Seven grams of 3,5-dibromoanthranilic acid[9] was fused with 4.1 g. of urea at 140° for about eight hours. The mass resulting on cooling was refluxed with ether, and the insoluble residue extracted successively with five 40-cc. portions of hot nitrobenzene. On allowing these extracts to cool, 6,8-dibromobenzoylene urea crystallized in small yellow needles, the melting points of the succeeding fractions varying from 293 to 295°. This material was collected, washed with ether and dried, the total yield being 5.6 g.

The yields were found to vary considerably with the temperature and duration of heating. In place of the ether and nitrobenzene extractions outlined above two treatments, each with 50 cc. of boiling acetone, in which the product is quite insoluble, may be substituted. The residue from this procedure was dissolved in a large excess of boiling lithium hydroxide solution, filtered and the filtrate acidified with dilute hydrochloric acid. The gelatinous precipitate that separated was collected, washed with water, dried and crystallized twice from hot glycol, yielding glistening, light yellow needles of 6,8-dibromobenzoylene urea, m. p. 305–306° corr.

Anal.[10] Calcd. for $C_8H_4O_2N_2Br_2$: Br, 49.97. Found: Br, 49.72, 49.86.

6-Bromobenzoylene urea was similarly obtained by fusing 7 g. of 5-bromoanthranilic acid[9] with 4.5 g. of urea. The brown porous solid that resulted was extracted with a hot solution of 2 g. of sodium hydroxide in 300 cc. of water, and the clear filtered extract acidified with hydrochloric acid, when the product separated as a thick flocculent precipitate. The compound was collected and dried and amounted to 6.6 g. of a yellow powder which did not crystallize satisfactorily from various solvents. Its hot saturated solution in dilute sodium hydroxide was allowed to crystallize, and the separated sodium salt redissolved in hot water and decomposed with acetic acid, which precipitated the 6-bromobenzoylene urea as a granular, light yellow solid, m. p. 357–358° corr. (dec.).[11]

6,8-Dibromobenzoylene urea is insoluble in the usual organic solvents and requires the use of high-boiling solvents in order to dissolve it. From its solution in cold concentrated sulfuric acid water precipitates it unchanged. Crystallization from glacial acetic acid was unsatisfactory, but crystallization from glycol is a convenient means of rapidly obtaining the pure substance. The products from both of the methods of preparation, *i. e.*, from dinitrobenzoylene urea and from dibromoanthranilic acid, were each subjected to such processes of purification as extraction of alkali-soluble impurities with sodium hydroxide and crystallization from nitrobenzene or an ethyl benzoate–alcohol mixture, and the preparations compared. In all cases they were identical and mixed melting points (305° corr.) between them showed no depression. Repeated attempts to determine the bromine content of these various preparations, using the method of Carius, gave low and inconsistent results.

Salts of 6,8-dibromobenzoylene urea with the alkali metals result directly on treating the free dibromo compound with aqueous solutions of the alkali hydroxides.

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(9) Wheeler and Oates, THIS JOURNAL, 32, 772 (1910).

(10) Micro-Pregl determinations by Mr. R. S. Wobus.

(11) Haslinger, *Ber.*, 41, 1453 (1908), gives m. p. 354°.

Strangely enough, the sodium salt is practically insoluble in water, and is by far the least soluble member of the group. The lithium salt, however, is somewhat more soluble and affords a convenient means of precipitating the sodium salt of dibromobenzoylene urea directly from aqueous solutions of sodium salts. A reagent was prepared by treating a mixture of 0.1 g. of dibromobenzoylene urea and 0.3 g. of lithium hydroxide with 5 cc. of water, heating to the boiling point, and diluting with 55 cc. of hot water. The suspension thus formed was boiled for a minute, when an almost clear solution resulted; this was stoppered and allowed to stand overnight and then filtered repeatedly until lithium carbonate ceased to precipitate and cloud the solution.

Half molar ($M/2$) solutions of cesium nitrate, rubidium chloride, potassium chloride, and sodium chloride were each diluted with an equal volume of the reagent: the sodium chloride solution became turbid and a white crystalline precipitate consisting of minute needles separated almost immediately; the other solutions remained clear. Molar solutions behaved similarly, excepting potassium chloride which precipitated within an hour; 2 M potassium chloride required only a few minutes. A $M/5$ sodium chloride solution was precipitated after a few minutes while a $M/10$ solution took a somewhat longer time to precipitate. A mixture of equal volumes of the $M/2$ sodium and potassium chloride solutions, when treated with a volume of the reagent, was also precipitated within a few minutes. These sodium salt precipitations are sometimes hastened by rolling the tubes between the hands; adding alcohol and shaking causes the precipitate to dissolve. Sodium nitrate, sodium sulfate, and sodium hydroxide solutions were likewise precipitated, but sodium salts of organic acids did not respond well to the test.

Ammonium hydroxide was not precipitated by the reagent but solutions of ammonium chloride and ammonium nitrate instantly gave white precipitates which, from their melting points, appear to be free dibromobenzoylene urea. The latter compound is very slightly soluble in boiling ammonium hydroxide (sp. gr. 0.9), from which solution a gelatinous precipitate separates slowly on cooling. Barium chloride, barium nitrate, and thallous sulfate, with the reagent, yielded heavy white precipitates.

In agreement with the failure of cesium nitrate to precipitate with the reagent, cesium hydroxide in aqueous solution dissolves considerably more dibromobenzoylene urea than does lithium hydroxide. A saturated solution, prepared by using an excess of cesium hydroxide, precipitated solutions of lithium chloride and lithium hydroxide within a few minutes, and acted in other respects like the solution of the dibromo compound in lithium hydroxide. It rapidly precipitated $M/10$ sodium chloride, while $M/2$ solutions of rubidium chloride and potassium chloride were precipitated slowly.

When the reagent in lithium hydroxide was allowed to stand for a few days it turned yellow to orange in color and gradually lost its power of precipitating sodium salts.

Sodium 6,8-dibromobenzoylene urea, precipitated by adding sodium hydroxide to a solution of the dibromo compound in aqueous lithium hydroxide, was collected, washed with water, and dried at 100° for two hours. Thus obtained, the salt forms a white powder consisting of microscopic hair-like needles, and has the composition of a monohydrate. It is insoluble in water or alcohol, slightly soluble in hot water, and soluble in dilute (1:1) alcohol. Attempts to determine its solubility in water at 25° gave consecutively lower results and indicated that a slight hydrolysis of the sample was taking place; the initial figure was 42 mg. of dissolved solids per 100 cc. of saturated solution. The compound becomes anhydrous during five days at 100°, or after twenty hours at 140°. When dried at 300° it decomposed. The analyses were made with four different preparations.

Anal. Calcd. for $C_8H_3O_2N_2Br_2NaH_2O$: Na, 6.39; H_2O, 5.01. Found: Na, 6.33, 6.34, H_2O, 4.87; Na, 6.06; Na, 6.22, 6.32; Na, 6.42, 6.25, H_2O, 5.07.

Lithium 6,8-dibromobenzoylene urea was obtained as a white solid on warming dibromobenzoylene urea with a small amount of aqueous lithium hydroxide solution. It is fairly soluble in water but, like the sodium salt, more soluble in dilute alcohol. Saturated solutions in water or dilute alcohol slowly deposited the salt in rosets of slender white needles. The compound was collected, washed with water and dried at 100°. Four analyses made with both the solid and crystallized material from different preparations gave results varying from 1.46 to 2.96% lithium; the mean of these four determinations is given.

Anal. Calcd. for $C_8H_3O_2N_2Br_2Li$: Li, 2.13. Found: Li, 2.16.

Preparation of 3-ethyl-6,8-dibromobenzoylene urea, $NC_2H_5COC_6H_2Br_2NHCO$.—One gram of dibromobenzoylene urea mixed with 0.4 g. of lithium hydroxide was treated with 60 cc. of water, boiled, and diluted with 60 cc. of alcohol. Five cc. of ethyl iodide was added and the clear solution refluxed on a steam-bath for ten hours, after which the alcohol was removed by evaporation and the resulting generally acidic mixture diluted with 30 cc. of water. Complete precipitation was assured by the addition of a few cc. of hydrochloric acid, and the 1.1 g. of precipitate which had separated was collected, washed with water, dried, and extracted with a hot solution of 1 g. of sodium hydroxide in 80 cc. of water. The alkaline solution was filtered from undissolved sodium salts, and the 3-ethyl derivative precipitated by acidifying the fitrate with hydrochloric acid. The product was removed by filtration, washed with water, and dried, and amounted to about 0.9 g. It was dissolved in 60 cc. of hot glycol, filtered and allowed to crystallize, when it separated in lustrous white satiny needles, m. p. 251° corr. The compound is sparingly soluble in hot alcohol from which it crystallizes in long thin needles on cooling. Hot concentrated hydrochloric acid is without effect, but cold concentrated sulfuric acid dissolves it readily to give a solution from which water precipitates it unchanged. It is soluble in warm solutions of sodium hydroxide, needles of the sodium salt separating slowly on cooling. For analysis the products from two different preparations were crystallized from glycol, washed with alcohol, and dried at 100°. The sodium salt was washed with cold water and dried at 100° for four days.

Anal. Calcd. for $C_{10}H_8O_2N_2Br_2$: Br, 45.94. Found: Br (Carius), 45.17, 44.45. Calcd. for $C_{10}H_7O_2N_2Br_2Na$: Na, 6.22. Found: Na, 6.40.

The same compound was obtained when a solution of dibromobenzoylene urea and potassium hydroxide in warm glycol was treated with ethyl iodide, although the latter is practically immiscible with glycol. By the action of dimethyl sulfate on the dibromo compound suspended in cold aqueous solutions of sodium or potassium hydroxide, a supposed 3-methyl derivative, m. p. 268° corr., and only slightly soluble in sodium hydroxide, resulted. With *n*-propyl iodide and lithium hydroxide in dilute *n*-propyl alcohol, a probable 3-*n*-propyl derivative, m. p. 225° corr., was formed.

Summary

By reduction, diazotization and a Sandmeyer reaction, the dinitro derivative resulting from the direct nitration of benzoylene urea has been converted into a dibromobenzoylene urea identical with the 6,8-dibromobenzoylene urea obtained by fusing 3,5-dibromoanthranilic acid with urea. The dinitro compound is, therefore, 6,8-dinitrobenzoylene urea.

On fusion with urea, 5-bromo- and 3,5-dibromoanthranilic acids yield the corresponding substituted benzoylene ureas; the analogous nitro- and dinitroanthranilic acids are not affected by this treatment.

Whereas 6,8-dinitrobenzoylene urea cannot be alkylated, 6,8-dibromo-

benzoylene urea undergoes alkylation to form monoalkyl derivatives. Especially characteristic of 6,8-dibromobenzoylene urea is its insolubility in the ordinary caustic alkalies, and the formation of a sparingly soluble sodium salt which can be precipitated from aqueous solutions at room temperature. This salt offers possibilities to investigators who are interested in the microchemical detection of sodium.

CLEVELAND, OHIO

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

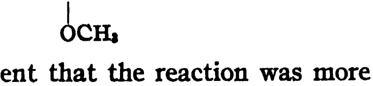
The Molecular Rearrangement of Alpha,Beta-Unsaturated Ethers[1]

BY WALTER M. LAUER AND MARVIN A. SPIELMAN[2]

It has long been known that certain α,β-unsaturated ethers rearrange on heating to form ketones. For the first example we are indebted to Claisen,[3] who found that α-ethoxystyrene readily forms phenyl propyl ketone "on short superheating such as boiling for a few hours under two atmospheres' pressure." Only a few such rearrangements have been recorded,[4] and the reaction is not general, since ethyl β-ethoxycrotonate, α-methoxymesityl oxide and phenyl vinyl ether, substances which might be expected to rearrange, failed to show such behavior.[5]

Previous studies have been confined to the establishment of rearrangement while the present one was undertaken in order to bring into sharper relief certain features dealing with the mechanism of the transformation. The α-alkoxy-styrenes lent themselves admirably to this purpose in view of the ease with which they may be prepared and the simplicity of the products which they form.

A. The Course of the Reaction.—When α-methoxystyrene was heated to temperatures in the neighborhood of 250–275° for an hour or more the chief product was always propiophenone formed by the normal rearrangement



$$\underset{\displaystyle OCH_3}{C_6H_5\overset{}{C}}{=}CH_2 \longrightarrow C_6H_5COCH_2CH_3 \qquad (1)$$

but it was also evident that the reaction was more complicated than we had anticipated. On unsealing the tube in which the rearrangement was carried out the presence of a combustible gas was noted, and after isolation of the propiophenone there remained a residue from which a colorless crystalline substance melting at 104.5° was isolated.

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[1] The work described in this paper constituted part of the thesis submitted to the graduate faculty of the University of Minnesota by Marvin A. Spielman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in June, 1933.

[2] Du Pont Fellow in Chemistry 1932–1933.

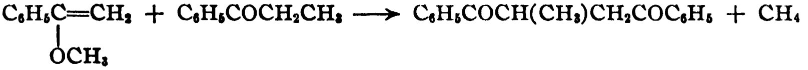
[3] Claisen, *Ber.*, **29**, 2931 (1896).

[4] Claisen and Haase, *ibid.*, **33**, 3778 (1900); Claisen, *ibid.*, **45**, 3157 (1912); Haller, *Compt. rend.*, **136**, 788 (1903); Staudinger and Ruzicka, *Helv. Chim. Acta.*, **7**, 386 (1924); Wislicenus and Schroeter, *Ann.*, **424**, 215 (1921).

[5] Wislicenus, *Ber.*, **33**, 1469 (1900); Pauly and Lieck, *ibid.*, **33**, 503 (1900); Powell with Adams, THIS JOURNAL, **42**, 646 (1920); Lauer and Spielman, *ibid.*, **55**, 1572 (1933).

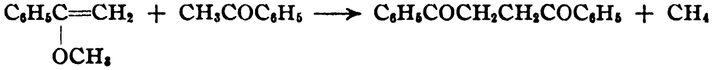
The molecular formula of this solid was established as $C_{17}H_{16}O_2$ and analysis by means of the Grignard machine[6] showed no active hydrogen, but two moles of methylmagnesium iodide were consumed per mole of compound. It formed a dioxime and on boiling with concentrated hydrochloric acid it lost one molecule of water to form a substance $C_{17}H_{14}O$ which upon analysis in the Grignard machine showed neither active hydrogen nor functional groups. The properties are those of a γ-diketone and that the compound $C_{17}H_{16}O_2$ was 1,2-dibenzoylpropane[7] was shown by comparison with a sample synthesized from benzoylacetic ester, α-bromopropiophenone and sodium ethylate, followed by hydrolysis of the resultant ester. This compound $C_{17}H_{14}O$ was therefore 2,5-diphenyl-3-methylfuran.

The origin of 1,2-dibenzoylpropane was indeed puzzling and we were finally forced to the conclusion that it resulted from the action of α-methoxystyrene upon its rearrangement product, propiophenone, with the elimination of methane.



$$\underset{\displaystyle OCH_3}{C_6H_5C}{=}CH_2 + C_6H_5COCH_2CH_3 \longrightarrow C_6H_5COCH(CH_3)CH_2COC_6H_5 + CH_4 \qquad (2)$$

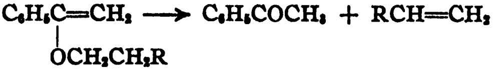
The evidence is as follows: first, propiophenone when heated alone did not yield these products but was recovered unchanged. Second, by heating α-methoxystyrene with a large excess of acetophenone, diphenacyl, a known compound was obtained.



$$\underset{\displaystyle OCH_3}{C_6H_5C}{=}CH_2 + CH_3COC_6H_5 \longrightarrow C_6H_5COCH_2CH_2COC_6H_5 + CH_4 \qquad (2a)$$

This was found to be identical with a synthetic sample.[8] Third, diphenacyl also resulted when α-ethoxystyrene was heated with acetophenone as did 1,2-dibenzoylpropane when it was heated with propiophenone. Fourth, the gas formed in the reactions involving α-methoxystyrene was analyzed and found to be methane, uncontaminated with other hydrocarbons or hydrogen. When α-ethoxystyrene was heated the gas was ethane containing 6% of ethylene; in the case of α-*n*-propoxystyrene it was propane containing 15.7% of propylene. Similarly, α-isoamyloxystyrene yielded two liquid hydrocarbons, isopentane and isopentene.

The occurrence of unsaturated hydrocarbons indicates another side reaction of a not unexpected type.



$$\underset{\displaystyle OCH_2CH_2R}{C_6H_5C}{=}CH_2 \longrightarrow C_6H_5COCH_3 + RCH{=}CH_2 \qquad (3)$$

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[6] Kohler, Stone and Fuson, THIS JOURNAL, 49, 3184 (1927); Kohler and Richtmyer, *ibid.*, 52, 3737 (1930).

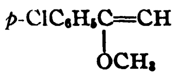
[7] Lutz and Taylor, *ibid.*, 55, 1175 (1933), have recently obtained this substance by the reduction of dibenzoylmethylethylene. The melting point (105° corr.) is in agreement with ours.

[8] Kapf and Paal, *Ber.*, 21, 3056 (1888).

The unchanged alkoxystyrene reacting with the acetophenone so produced should yield diphenacyl by reaction 2a. Acetophenone and diphenacyl, along with isoenanthophenone, the normal rearrangement product, were actually isolated from the reaction mixture obtained by heating α-isoamyloxystyrene. The low percentages of unsaturated hydrocarbons show that this side reaction does not play an important role unless the size of the alkyl groups is large.

A number of α-β-unsaturated ethers (see experimental part) were examined. It is noteworthy that no isomerization of radicals took place during rearrangement and that there was γ-diketone formation in all cases wherein rearrangement occurred.

B. The Mechanism of the Reaction.—In developing a mechanism for the rearrangement (Reaction 1) the first possibility considered was that of a purely intramolecular change in which the wandering group at no time becomes free from the sphere of influence of the parent molecule.[9] This was definitely eliminated by means of the following experiment. Two enol ethers I and II were rearranged simultaneously in mutual solution.



$p\text{-}ClC_6H_4C(OCH_3)=CH_2$

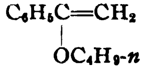
I

$p\text{-}ClC_6H_4COCH_2CH_3$

III

$C_6H_5COCH_2CH_3$

V



$C_6H_5C(OC_4H_9\text{-}n)=CH_2$

II

$C_6H_5COCH_2C_4H_9\text{-}n$

IV

$p\text{-}ClC_6H_4COCH_2C_4H_9\text{-}n$

VI

On the basis of a strictly intramolecular change but two products of rearrangement III and IV should result. On the other hand, if the mechanism were such that a radical might wander from one molecule to another at some stage of the process, two additional products V and VI should be engendered. In view of side reactions (2) and (3) the reaction mixture would be expected to possess considerable complexity (there is the possibility of fifteen components, exclusively of gases and starting materials) but the choice of ethers made the isolation of propiophenone V feasible on account of its comparatively low boiling point, granting the practicability of separating it from the acetophenone formed from α-*n*-butoxystyrene II by reaction (3). The two ethers I and II were accordingly heated in the customary manner and the lowest boiling fraction was converted to a mixture of semicarbazones. After a series of systematic crystallizations the semicarbazone of propiophenone V was isolated in pure form. A strictly intramolecular mechanism therefore becomes untenable.

A common manner of interpreting many molecular rearrangements involves simple dissociation into mobile ions or radicals.[10] Such a process

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(9) This is true in the case of the benzimido phenyl esters. Chapman, *J. Chem. Soc.*, **127**, 1992 (1925).

(10) For leading references on rearrangements see Whitmore, THIS JOURNAL, **54**, 3274 (1932).

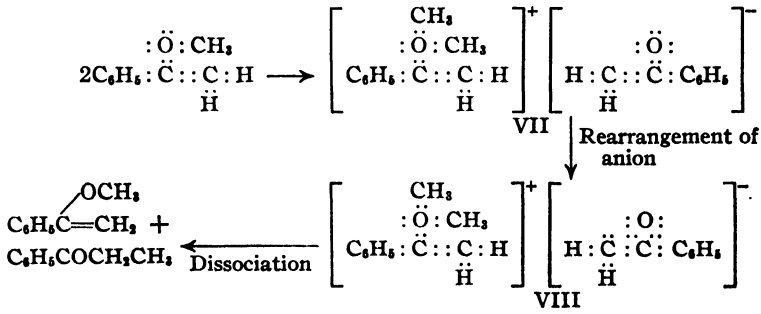
would proceed at a velocity proportional to the concentration of the enol ether and thus exhibit the kinetic behavior of a first order reaction. Kinetic studies[11] have shown that we are dealing with a homogeneous reaction of the second order. The complete absence of certain products formed by the indiscriminate union of free radicals (diphenacyl and ethane in reaction 1) also renders their intermediary existence highly improbable.

Since the rearrangment represents a second order reaction we are forced inevitably to the conclusion that the collision of two activated ether molecules results in the formation of a complex body, thus

$$\text{2 Enol Ether} \rightleftarrows \text{[Complex]} \longrightarrow \text{2 Ketone, or Enol Ether + Ketone}$$

The experiment demonstrating the intermolecular transfer of radicals imposes, however, an added restriction. In the complex the two potentially migrant groups must be equivalent.

Van Alphen[12] has advanced a theory accounting for phenol ether rearrangements in which oxonium intermediates are involved. This is compatible with our experimental facts if we assume that the molecule adding to the ether is a second molecule of the ether itself.[13] Accordingly, we are inclined to formulate the rearrangement of the α,β-unsaturated ethers in the following manner. The first step represents the formation of an oxonium complex VII. Transfer of a pair of electrons in the anionoid part of the complex shifts the seat of activity from the oxygen to the α-carbon atom as indicated in VIII. Dissociation would then be expected to yield the products propiophenone and α-methoxystyrene.[14]



The transfer of a radical from one molecule to another which seemed so puzzling at first would be predicted on the basis of this mechanism. Thus, the addition of α-*n*-butoxystyrene to *p*-chloro-α-methoxystyrene would yield the complex IX

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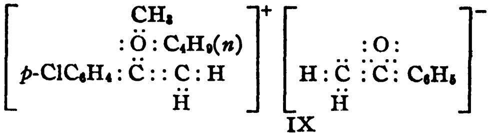
(11) MacDougall, Lauer and Spielman, THIS JOURNAL, 55, 4089 (1933).

(12) Van Alphen, *Rec. trav. chim.*, 46, 804 (1927).

(13) Niederl and Storch, THIS JOURNAL, 55, 284 (1933), in discussing certain phenol ether rearrangements perhaps imply this in their reference to "the formation of oxonium compounds between identical ether molecules" and "transitory bimolecular compounds of the quinhydrone type."

(14) Strict analogy with the Van Alphen mechanism requires that the rearrangement take place in the cationoid part of the complex. Between such a view and ours there is at present no means of experimental differentiation.



$$\left[\begin{array}{c} \mathrm{CH_3} \\ :\ddot{\mathrm{O}}:\mathrm{C_4H_9}(n) \\ p\text{-}\mathrm{ClC_6H_4}:\ddot{\mathrm{C}}::\mathrm{C}:\mathrm{H} \\ \ddot{\mathrm{H}} \end{array}\right]^+ \left[\begin{array}{c} :\mathrm{O}: \\ \mathrm{H}:\ddot{\mathrm{C}}:\ddot{\mathrm{C}}:\mathrm{C_6H_5} \\ \ddot{\mathrm{H}} \end{array}\right]^-$$

IX

in which it is seen that the alkyl groups are equivalent. Dissociation would then yield the mixture of products actually encountered.

Experimental Part

Synthesis of Materials.—The ethers used in this work were prepared by a method previously reported.[15] New β-bromo ethers are shown in Table I. All are colorless oily liquids having a fragrant aromatic odor. These on distillation from powdered potassium hydroxide yielded the desired enol ether. Usually two distillations at 100 mm. were necessary, and at a suggestion from Chalmers[16] soda lime has been used with the alkali. It has the virtue of preventing fusion and thus prolongs the life of the flask. Of the enol ethers, two were new.

TABLE I

β-BROMO ETHERS

Compound	Formula	Yield, %	B. p., °C.	Analyses, Br % Calcd.	Found
$C_6H_5CH(OCH_3)CH_2Br$	$C_9H_{11}OBr$	65	117–118 (15 mm.)	37.16	37.32
p-$ClC_6H_4CH(OCH_3)CH_2Br$	$C_9H_{10}OBrCl$	51	154–156 (26 mm.)	[a]	
$C_6H_5CH(OC_3H_7\text{-}n)CH_2Br$	$C_{11}H_{15}OBr$	66	146–148 (27 mm.)	32.86	32.79
$C_6H_5CH(OC_4H_9\text{-}n)CH_2Br$	$C_{12}H_{17}OBr$	57	165–166 (32 mm.)	31.13	30.56
$C_6H_5CH(OC_5H_{11}\text{-iso})CH_2Br$	$C_{13}H_{19}OBr$	81	140–143 (12 mm.)	28.47	29.06

[a] Calcd.: C, 43.3; H, 4.04. Found: C, 43.5; H, 4.4.

α-n-Butoxystyrene.—Yield, 70%; b. p. 134.5–135.5° (26 mm.); n^{25}_{D} 1.5193.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.1. Found: C, 81.4, 81.4; H, 9.0, 8.7.

p-Chloro-α-methoxystyrene.—Yield, 59%; b. p. 118–121° (23 mm.); n^{28}_{D} 1.5510.

Anal. Calcd. for C_9H_9OCl: Cl, 21.05. Found: Cl, 20.69, 20.92.

The compound is a very fragrant oil. Treatment with semicarbazide hydrochloride and sodium acetate in dilute alcohol gave p-chloroacetophenone semicarbazone: needles, m. p. 202–204°.

Anal. Calcd. for $C_9H_{10}N_3OCl$: C, 51.0; H, 4.8; Cl, 16.8. Found: C, 50.8; H, 4.7; Cl, 16.8.

The Rearrangement and Condensation Reactions

α-Methoxystyrene.—Twenty grams was sealed in a Carius tube and heated for 2 hours in a bomb furnace at approximately 300°. When the tube was unsealed considerable pressure was observed. The contents were transferred to a Claisen flask and distilled. After a forerun of less than 1 g., a single fraction of 13 g. came over at 98–103° (15 mm.). There was a clear brown residue of 5.7 g.

The main fraction was converted to the semicarbazone which after one crystallization melted at 173–173.5°. This is correct for propiophenone semicarbazone. A mixed melting point was not depressed.

The residue remaining after distillation was taken up in 15 cc. of methanol which caused immediate crystallization. After one recrystallization the product weighed 2.0

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(15) Lauer and Spielman, THIS JOURNAL, 53, 1533 (1931); Swallen and Boord, *ibid.*, 52, 651 (1930); Dykstra, Lewis and Boord, *ibid.*, 52, 3396 (1930).

(16) Chalmers, *Canadian J. Res.*, 7, 464 (1932).

g. and melted at 102–103°. Several crystallizations from petroleum ether gave colorless hexagonal plates; m. p. 104–104.5°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4; mol. wt. 252. Found: C, 80.8, 80.7; H, 6.3, 6.3; mol. wt. 258.

In the Grignard machine the substance reacted with 2.12 moles of methylmagnesium iodide and liberated a negligible amount of methane. The dioxime was prepared by the use of free hydroxylamine in methanol; snow-white needles; m. p. 166–167°.

Anal. Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.3; H, 6.4. Found: C, 72.7; H, 6.3.

Dehydration to 2,5-diphenyl-3-methylfuran proceeded quantitatively on boiling for half an hour in concd. hydrochloric acid; m. p. 57–58°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 87.3, 87.2; H, 6.0, 6.1.

A sample of 1,2-dibenzoylpropane was synthesized by condensing α-bromopropiophenone with ethyl benzoylacetate and hydrolyzing the resultant ester. The directions are those used by Kapf and Paal[8] in the preparation of diphenacyl; m. p. and mixed m. p. 104–104.5°.

Condensation of α-Methoxystyrene and Acetophenone.—Ten grams of the ether and 20 g. of the ketone were heated to 300° for two hours. Unsealing revealed considerable pressure. After distillation a non-volatile fraction of 2.2 g. remained. Washing with ether and crystallization from ethanol yielded pure diphenacyl; m. p. and mixed m. p. 142–144°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found C, 80.7; H, 6.2.

The gas formed in the same condensation reaction was collected and analyzed in the conventional Orsat–Lunge apparatus. Methane was identified by its contraction ratio, which is the ratio of the contraction on burning to the volume of carbon dioxide formed. Calcd.: 2.00. Found: 2.02. No hydrogen or unsaturated hydrocarbons could be detected.

α-Ethoxystyrene (25 g.) was similarly heated to 300° for one hour. The main product weighed 14.4 g. and boiled at 115–121° (20 mm.). The semicarbazone melted at 183–185° and mixture with butyrophenone semicarbazone caused no depression. The residue of 1,2-dibenzoylbutane could not be induced to crystallize. Distillation gave a 1.5 g. fraction; b. p. 234–245° (20 mm.); n^{25}_{D} 1.5795. It was a pale yellow extremely viscous liquid.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.7. Found: C, 81.5, 81.4; H, 7.0, 6.9.

The gaseous products from the condensation proved to be ethane containing 6% of ethylene. After removal of the latter the contraction ratio was found to be 1.23; theory requires 1.25.

α-*n*-Propoxystyrene.—This gave a poor yield (30%) of *n*-valerophenone boiling at 138–143° (28 mm.). The semicarbazone melted at 162.5–163.5° and a mixed m. p. with a sample prepared from the ketone obtained by oxidizing phenyl-*n*-butylcarbinol was not depressed.

The condensation product, presumably 1,2-dibenzoylpentane, could not be isolated analytically pure. Propane was formed. Calcd. contraction ratio: 1.00. Found: 1.07. It contained 15.7% propylene.

α-*n*-Butoxystyrene.—From 5 g. heated to 300° for one hour, 3.7 g. of *n*-caprophenone of m. p. 24–26° was obtained. The semicarbazone melted at 131–132°. Other products were not characterized.

***p*-Chloro-α-methoxystyrene.**—Fifteen grams heated in the usual way gave 10.2 g. of *p*-chloropropiophenone which boiled at 134–137° (31 mm.). The semicarbazone formed well-developed needles; m. p. 175–176°.

Anal. Calcd. for $C_{10}H_{12}N_3OCl$: C, 53.2; H, 5.3; Cl, 15.7. Found: C, 53.0; H, 5.4; Cl, 15.8.

From the residue about 1.8 g. of a gummy solid was obtained. This was reduced to 0.6 g. before analytically pure 1,2-di-(*p*-chlorbenzoyl)-propane was isolated as snow-white needles melting at 116.5–117.0°.

Anal. Calcd. for $C_{17}H_{14}O_2Cl_2$: C, 63.6; H, 4.4; Cl, 22.1. Found: C, 63.3; H, 4.6; Cl, 22.2.

α-Isoamyloxystyrene.—Twenty grams was heated to 300° for seventy-five minutes. The tube was cooled in ice and on unsealing little pressure was observed. The product had the odor of crude gasoline. Distillation gave the following fractions: A, 29–40°, 1.2 g.; B, 90–115° (17 mm.), 1.9 g.; C, 122–143° (17 mm.) 1.8 g.; D, 143–147° (17 mm.), 11.0 g.; E, to 223° (5 mm.), 2.9 g.

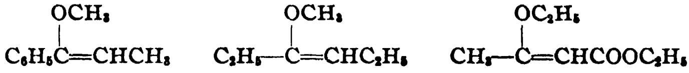
Fraction A was shaken with 70% sulfuric acid to remove isopentene, dried over calcium chloride and distilled, b. p. 28.5–30.0°, n^{20}_{D} 1.3570. The values for isopentane taken from Beilstein are b. p. 27.97 to 30.0°, n^{20}_{D} 1.35485. Fractions B and C were redistilled and 1.7 g. of acetophenone was obtained; b. p. 93–105° (17 mm.), m. p. and mixed m. p. of the semicarbazone 198–202°. Fraction D and the higher boiling parts of B and C were combined and redistilled. Practically all came over as pure isoenanthophenone (phenyl isohexyl ketone); b. p. 145–148° (18 mm.); n^{26}_{D} 1.5067.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.8, 81.6; H, 9.4, 9.4.

The semicarbazone formed colorless leaflets; m. p. 144–145°.

Anal. Calcd. for $C_{14}H_{21}N_3O$: C, 68.0; H, 8.6. Found: C, 68.0; H, 8.7.

Fraction E was seeded with a single crystal of diphenacyl and placed in the ice box. About 5 mg. was obtained; m. p. and mixed m. p. 143–145°.



The ethers, $C_6H_5\overset{\displaystyle OCH_3}{\overset{|}{C}}{=}CHCH_3$ $C_2H_5{-}\overset{\displaystyle OCH_3}{\overset{|}{C}}{=}CHC_2H_5$ $CH_3{-}\overset{\displaystyle OC_2H_5}{\overset{|}{C}}{=}CHCOOC_2H_5$ failed to rearrange under the conditions studied. They were recovered unchanged except α-methoxy-β-methylstyrene which was shown, on the basis of a Zeisel determination, to be approximately half decomposed after four and one-half hours. No ketone could be found in the tar-like mixture.

Intermolecular Transfer of Radicals.—Ten grams each of *p*-chloro-α-methoxystyrene and α-*n*-butoxystyrene were heated together to 265° for three hours. The material was placed in a modified Claisen flask with a 15-cm. indented column and distilled. The first fraction came over at 94–101–105° (16 mm.). The temperature then rose rapidly and further fractions were not examined. The distillate (1.7 g.) gave a negative Beilstein test for chlorine. It was converted to a mixture of semicarbazones which was subjected to a systematic series of twenty-six crystallizations from dilute alcohol to which was added from time to time a little semicarbazide hydrochloride and sodium acetate to suppress hydrolysis. At the conclusion of the separation 0.1 g. of acetophenone semicarbazone was isolated: m. p. and mixed m. p. 199–201°. A mixed fraction of 0.1 g. remained: m. p. 144–158°. The important part (0.11 g.) was pure propiophenone semicarbazone which melted at 172–174° alone and when mixed with an authentic sample. It was mixed with the semicarbazones derived from each of the lower phenyl ketones and marked depressions were observed in every case. A blank experiment was run on the unheated components and the first drop distilled at 110° (14 mm.). Experience gained in numerous practice separations leads to the opinion that the reaction mixture contained at least 1 gram of propiophenone.

Summary

1. Certain alkoxystyrenes rearrange upon heating to form ketones.

2. The unchanged ether condenses with its rearrangement product: a hydrocarbon is eliminated and a γ-diketone results.

3. Not all enol ethers undergo these reactions.

4. A mechanism for the transformation is advanced. It involves complex formation between two ether molecules followed by rearrangement in either of the two parts of the complex body.

MINNEAPOLIS, MINNESOTA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Syntheses in the Olefin Series. V. Completing the Survey of the Hexenes and Including Certain Heptenes and Octenes[1]

BY IMAN SCHURMAN[2] AND CECIL E. BOORD

In the third paper of this series Schmitt[3] and one of us in a survey of the hexenes, described eleven of the thirteen isomers as prepared by the bromo ether method. This method is not applicable to the tetra-alkylethylenes, type V, or to the *tert*-alkylethylenes of type I. It has seemed desirable, therefore, to seek other methods for the preparation of tetramethylethylene, the highest boiling hexene, and *tert*-butylethylene, the lowest boiling member of this family, and to measure their physical constants under conditions wholly comparable with those used for the other isomers.

Tetramethylethylene has been described by numerous investigators, its physical constants having been measured under widely varying conditions. It is most conveniently prepared by the dehydration of isopropyldimethylcarbinol, this method yielding also *as*-isopropylmethylethylene in smaller amounts.[4]

$$(CH_3)_2COH—CH(CH_3)_2 \longrightarrow \begin{cases} (CH_3)_2C{=}C(CH_3)_2 \\ (CH_3)_2CH—(CH_3)C{=}CH_2 \end{cases}$$

For the present purpose the above carbinol was dehydrated over anhydrous oxalic acid, the two heptenes being obtained in yields of 80 and 20%, respectively. Their physical constants were measured under the conditions previously used in this series.

It is well known that *tert*-butylmethylcarbinol (pinacolin alcohol) does not yield the normally expected *tert*-butylethylene as the principal dehydration product. Alcohols of this type upon dehydration undergo a skeletal rearrangement. Such rearrangements have been frequently studied, and most recently by Whitmore and his co-workers,[5] who found only 3% of

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(1) (a) For the earlier papers of this series see Soday and Boord, THIS JOURNAL, **55**, 3293 (1933). (b) Presented before the Organic Division of the American Chemical Society in Washington, March, 1933, and before the Chemical Section of the Ohio Academy of Science May, 1933.

(2) Research Associate under a Grant-in-Aid from the National Research Council, to whom our best thanks are due for making this work possible.

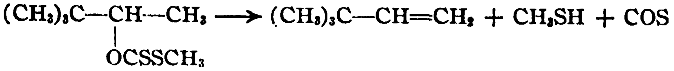
(3) Schmitt and Boord, THIS JOURNAL, **54**, 751 (1932).

(4) (a) Henry, *Bull. soc. chim. Belg.*, **22**, 140 (1907); (b) Couturier, *Bull. soc. chim.*, [4] **9**, 898 (1911).

(5) Whitmore, THIS JOURNAL, **54**, 3274 (1932); Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933); Whitmore and Meunier, *ibid.*, **55**, 3721 (1933).

tert-butylethylene among the dehydration products of the above carbinol.

The one method which above all others has proved most successful for the preparation of *tert*-butylethylene is the decomposition of the methyl xanthate of *tert*-butylmethylcarbinol.



$$(CH_3)_3C-\underset{\displaystyle OCSSCH_3}{\underset{|}{C}H}-CH_3 \longrightarrow (CH_3)_3C-CH{=}CH_2 + CH_3SH + COS$$

Fomin and Sochanski[6] adapted the method first used by Tschugaeff[7] in an extended study of the terpenes, to this one case among the simple olefins. The results of these authors have been confirmed in every detail.

In the earlier papers of this series it has been pointed out, from time to time, that the β-olefins of type II boil lower than the corresponding saturated hydrocarbons. And it will be further shown, in a general paper now in preparation concerning the relation of the physical constants of the simple olefins to their structure, that this rule is general for the olefins of type II.

Faworski and Alexejewa,[8] by the action of alcoholic potassium hydroxide upon 2,2-dimethyl-3-bromopentane, obtained a heptene boiling at 84–86° which they designated as *s*-*tert*-butylmethylethylene. If this olefin has the boiling point indicated it forms a marked exception to the above rule. The question is raised, therefore, does the heptene described have the structure assigned? Edgar, Calingaert and Marker[9] found this method as well as the dehydration of 2,2-dimethyl-3-pentanol to yield a mixture of heptenes having a wide boiling range. Furthermore, this mixture upon hydrogenation did not give an individual heptane. It seems obvious that a rearrangement takes place during the dehydration of the latter carbinol analogous to that found in the case of the simpler pinacolin alcohol.

The heptene obtained by the decomposition of the methyl xanthate of *tert*-butylethylcarbinol was found to boil at 76.9° (760 mm.). Upon hydrogenation it yielded 2,2-dimethylpentane identical with that prepared by Edgar and his co-workers by the condensation of *n*-propylmagnesium bromide with *tert*-butyl chloride. One must conclude, therefore, that Faworski and Alexejewa's hydrocarbon was probably a mixture and that pure 4,4-dimethyl-2-pentene boils at the lower temperature indicated above and thus conforms to the rule.

The present authors have found the xanthic ester synthesis to be a method which may be depended upon to yield the *tert*-alkyl derivatives of ethylene true to structure. Advantage has been taken of this peculiarity of the method to extend the surveys being made of the hexene, heptene and octene families. The present paper describes: 3,3-dimethyl-1-butene, 3,3-dimethyl-1-pentene, 4,4-dimethyl-2-pentene, 4,4-dimethyl-2-hexene

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(6) Fomin and Sochanski, *Ber.*, **46**, 246 (1899).

(7) Tschugaeff, *ibid.*, **32**, 3332 (1899).

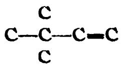
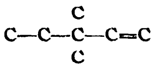
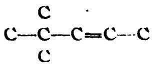
(8) Faworski and Alexejewa, *J. Russ. Phys.-Chem. Soc.*, **50**, 561 (1918).

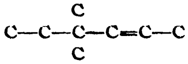
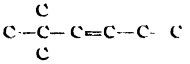
(9) Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1485 (1929).

and 2,2-dimethyl-3-hexene. The physical constants of these olefins are recorded in Table I.

TABLE I

PHYSICAL CONSTANTS OF THE OLEFINS

Structure	 $C-\overset{C}{\underset{C}{C}}-C=C$	 $C-C-\overset{C}{\underset{C}{C}}-C=C$	 $C-\overset{C}{\underset{C}{C}}-C=C-C$
Type	I	I	II
B. p., °C. at (mm.)	40.2-40.4(747) 41.0-41.2(760) 41.2[a](760)	76.0(745) 76.9(760)	75.0-75.1(739) 76.0-76.1(760) 84-86[b]
d_4^{20}	0.6510 0.6549_{4}^{18}[a]	0.6961	0.6881 0.7220[b]
n_D^{20}	1.3759 1.37667[a]	1.3991	1.3986
MR, obs.	29.76 29.53[a]	34.06	34.44
MR, calcd.	29.44	34.06	34.06

Structure	 $C-C-\overset{C}{\underset{C}{C}}-C=C-C$	 $C-\overset{C}{\underset{C}{C}}-C=C-C-C$
Type	II	II
B. p., °C. at (mm.)	103.5-104.1(739) 105.4-106.0(760)	99.0(750.5) 100.1(760)
d_4^{20}	0.7202	0.7048
n_D^{20}	1.4120	1.4068
MR, obs.	38.91	39.14
MR, calcd.	38.68	38.68

[a] Fomin and Sochanski, *Ber.*, **46**, 246 (1913).

[b] Faworski and Alexejewa, *J. Russ. Phys.-Chem. Soc.*, **50**, 561 (1920).

Experimental Part

Dehydration of Isopropyldimethylcarbinol.—Four moles (408 g.) of isopropyldimethylcarbinol and 1200 g. of anhydrous oxalic acid were heated on an oil-bath under a reflux condenser, at 100°, for about eight hours. The condenser was then turned down and the mixture distilled. The distillate was washed six times with ice water, dried over calcium chloride and distilled repeatedly over sodium. After several fractionations through a 46 × 1.3 cm. column, closely packed with carborundum, and using a ratio of return to take off of 10 to 1, the mixture of heptenes was separated chiefly into two fractions boiling at 55.0-55.4° (748 mm.) and 72.3-72.6° (747 mm.), respectively.

The high boiling isomer, tetramethylethylene (2,3-dimethyl-2-butene), showed the following physical constants: b. p. 72.3-72.6° (747 mm.), 72.9-73.2° (760 mm.); d_4^{20} 0.7081; n_D^{20} 1.41153, n_α^{20} 1.40867, n_β^{20} 1.41775; MR. obs. 29.49, calcd. 29.44; melting

TABLE II

METHYL XANTHATES OF SECONDARY CARBINOLS

Carbinol	B. p. (uncorr.), °C.	Yield, %	Methyl xanthates[a] B. p. (mm.) °C.		d_4^{20}	n_D^{20}	Yield, %	Olefin yield % on ester	Olefin yield % on carbinol
Methyl-*tert*-butyl	116-119	60	85-87	(6)	1.0255	1.5242	73.5	58	41.6
Methyl-*tert*-amyl	142-145	50	110-112	(8)	1.0235	1.5250	75.0	67	51.0
Ethyl-*tert*-butyl-	132-135	58	92-92.5	(5)	1.0014	1.5206	60.0	73	44.0
Ethyl-*tert*-amyl-	156-160	25	118-120	(8)	1.0160	1.5210	41.0	55	22.5
n-Propyl-*tert*-butyl-	151-155	57	112-114	(8)	0.9950	1.5122	63.0	63	40.0

[a] The methyl xanthates are completely decomposed when distilled under atmospheric pressure. Apparently they are partially decomposed when distilled under the low pressures indicated. The methyl xanthate of ethyl-*tert*-butylcarbinol upon analysis for sulfur gave 31.69 and 31.92%. The theoretical value is 31.09%.

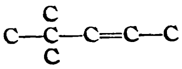
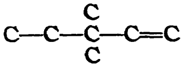
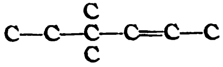
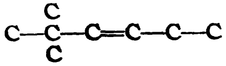
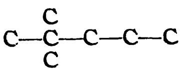
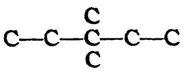
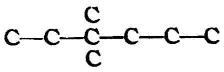
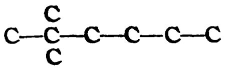
TABLE III

OLEFIN DIBROMIDES

Name	B. p., °C.	(mm.)	d_4^{20}	n_D^{20}	MR, (obs.)	MR, (calcd.)	Bromine, % Found	Bromine, % Calcd.
1,2-Dibromo-3,3-dimethylpentane	95.3–95.6	(10)	1.5615	1.5109	49.77	50.05	61.82	61.92
2,3-Dibromo-4,4-dimethylpentane	92.8–93.0	(14)	1.5538	1.5080	49.47	50.05	61.65	61.92
2,3-Dibromo-4,4-dimethylhexane	92.0–93.0	(4)	1.5148	1.5113	54.21	54.67	58.70	58.82
3,4-Dibromo-2,2-dimethylhexane	96.5–97.0	(8)	1.4856	1.5032	54.54	54.67	58.04	58.82

TABLE IV

HYDROGENATION OF OLEFINS

Olefin	Structure	 $C-\overset{C}{\underset{C}{C}}-C=C-C$	 $C-C-\overset{C}{\underset{C}{C}}-C=C$	 $C-C-\overset{C}{\underset{C}{C}}-C=C-C$	 $C-\overset{C}{\underset{C}{C}}-C=C-C-C$
	G.	12	10	8	12
Saturated hydrocarbons	Structure	 $C-\overset{C}{\underset{C}{C}}-C-C-C$	 $C-C-\overset{C}{\underset{C}{C}}-C-C$	 $C-C-\overset{C}{\underset{C}{C}}-C-C-C$	 $C-\overset{C}{\underset{C}{C}}-C-C-C-C$
	Yield, g.	10	7	6.5	9
	B. p., °C. (760)	78.8 78.9[a]	85.9–86.0 86.0[a]	110.7–111.2 111–112[b]	106.8–107.1 106–107[b]
	d_4^{20}	0.6736 0.6737[a]	0.6926 0.6934[a]	0.7078 0.7116[b]	0.6953 0.6967[b]
	n_D^{20}	1.3822 1.38233[a]	1.3910 1.39114[a]	1.3992 1.3998[b]	1.3930 1.3931[b]
	Mol. ref. Obs.	34.60 34.61[a]	34.35 34.32[a]	39.03 38.8[b]	39.17 39.0[b]
	Mol. ref. Calcd.	34.526	34.526	39.14	39.14

[a] Edgar and Calingaert, THIS JOURNAL, 51, 1540 (1929).

[b] Noller, *ibid.*, 51, 594–599 (1929).

point −76.4°.[10] The low boiling isomer, *as*-isopropylmethylethylene (2,3-dimethyl-1-butene), gave: b. p. 55.0–55.4° (748 mm.), 55.6–56.0° (760 mm.); d_4^{20} 0.6810; n_D^{20} 1.3899; MR (obs.) 29.27; calcd. 29.44; melting point −120 to −123°.

Methyl Xanthates.—One and one-tenth moles of metallic potassium was caused to react with an equivalent amount of *tert*-amyl alcohol dissolved in 1500 cc. of toluene, by boiling under a reflux condenser. One mole of the appropriate secondary carbinol was added to the hot solution, it being thus converted, according to Tschugaeff,[11] into the alcoholate. After cooling, 1.5 moles (115 g.) of carbon disulfide was slowly added causing the precipitation of the yellow potassium xanthate. Since much heat was evolved by this reaction the mixture was again cooled to room temperature and 1.1 moles (156 g.) of methyl iodide added and the mixture heated on the water-bath from four to five hours. After filtering, to remove the precipitated potassium iodide, the toluene and alcohol were distilled from the xanthic ester under a pressure of about 70 mm. The ester was then transferred to a modified Claisen flask and distilled under strongly diminished pressure. In later runs the methyl iodide was replaced by an equivalent amount of methyl sulfate with equally good results. The yields and physical constants of the methyl xanthates are recorded in Table II.

Decomposition of the Methyl Xanthates.—The purified ester was placed in a flask which was provided with a short upright condenser. The top of this condenser was in turn connected to the top of a coil condenser, set vertically, through which ice water was circulated. The receiver was immersed in a bath of ice and salt. By heating the flask gently the ester was slowly decomposed with a quiet ebullition.

The distillate was washed three times with strong potassium hydroxide solution, twice with ice water and then dried over calcium chloride. It was finally purified by distilling over a mixture of freshly cut sodium and potassium. The physical constants of the olefins prepared in this way are recorded in Table I.

Dibromides.—Ten or twelve grams of the olefin was dissolved in 50 cc. of chloroform and slowly treated with an equivalent amount of dry bromine dissolved in an equal volume of the same solvent. The bromination was carried out below 5° and in diffused light. The solvent was removed by distillation and the residual dibromides distilled under diminished pressure. The physical constants and analyses of the resulting dibromoparaffins are recorded in Table III.

Hydrogenation of the Olefins.—Ten or twelve grams of the olefin was dissolved in 75 cc. of ordinary alcohol and hydrogenated in a Burgess–Parr apparatus by the method of Voorhees and Adams.[12] The saturated hydrocarbon was precipitated by dilution with water, separated and washed with concentrated sulfuric acid to remove the last traces of water, alcohol and olefin. Final purification was effected by distillation from a modified Claisen flask having a 20.3 × 1.3 cm. Vigreux column "built in" to the side-arm. The physical constants of the saturated hydrocarbons are shown in Table IV in comparison with those previously recorded in the literature.

Summary

The physical constants of tetramethylethylene (2,3-dimethyl-2-butene) have been remeasured, under the conditions used for the isomeric hexenes, and those of *tert*-butylethylene (2,2-dimethyl-1-butene) confirmed, thus completing the survey of the hexenes.

The methyl xanthate synthesis has been extended to the preparation of

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(10) The authors are greatly indebted to Mr. Earl O. Long for the determination of the melting points of this and the following heptene.

(11) Tschugaeff, *J. Russ. Phys.-Chem. Soc.*, **36**, 1253 (1904), through *J. Chem. Soc.*, **88**, 166 (1905).

(12) Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

3,3-dimethyl-1-pentene, 4,4-dimethyl-2-pentene, 4,4-dimethyl-2-hexene and 2,2-dimethyl-3-hexene and their physical constants are recorded. These olefins are new.

As evidence that a skeletal rearrangement did not take place in the formation of these olefins, 4,4-dimethyl-2-pentene was hydrogenated to 2,2-dimethylpentane, 3,3-dimethyl-1-pentene to 3,3-dimethylpentane, 4,4-dimethyl-2-hexene to 3,3-dimethylhexane and 2,2-dimethyl-3-hexene to 2,2-dimethylhexane.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF BROWN UNIVERSITY]

Aliphatic Germanium Derivatives. III. Ethylgermanium Trihalides

BY E. A. FLOOD

Methods of preparation of ethylgermanium trihalides and some reactions of these compounds are described herein. In the preceding paper of this series it was pointed out that considerable difficulty is encountered in attempting to substitute a second bromine atom for an ethyl group in triethylgermanium bromide by the direct action of bromine.[1] It was therefore anticipated that the bromination of tetraethylgermane would not be a feasible method of obtaining monoethylgermanium derivatives. However, ethylgermanium triiodide can be obtained in almost quantitative yields from ethyl iodide and germanous iodide, which react according to the equation $C_2H_5I + GeI_2 = C_2H_5GeI_3$. Since germanium is readily extracted from its ore, germanite, as the volatile germanous sulfide which when treated with hydriodic acid yields GeI_2,[2] this method of preparing monoethylgermanium derivatives is simple and direct.

Ethylgermanium Triiodide, $C_2H_5GeI_3$.—When germanous iodide and an excess of ethyl iodide are heated together, in the absence of air, to a temperature of 110° reaction takes place over a period of several days with the formation of ethylgermanium triiodide, while if the reaction is carried out at a temperature of 140° a mixture of products is obtained, the chief constituents being germanium tetraiodide, unidentified gases and only very little ethylgermanium triiodide.

Preparation.—The following is a typical preparation of the triiodide from crude germanous iodide.

A mixture consisting of 18.5 g. of germanous iodide and 40 g. of ethyl iodide in an air-free sealed tube was heated to a temperature of 110° during three days. At the end of this period most of the solid had disappeared. The tube was opened and the liquid transferred to a vacuum fractionating apparatus in which the excess ethyl iodide was separated from the reaction product and the residual liquid product subjected to several fractional distillations *in vacuo*. Traces of iodine were removed from the impure triiodide during the second distillation by means of finely divided silver which had been previously placed in the apparatus. A small quantity of germanium tetraiodide and 23.5 g. of a high boiling yellow colored liquid were finally obtained. The liquid product was analyzed for iodine and germanium and thus shown to be ethylgermanium triiodide.

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[1] E. A. Flood, THIS JOURNAL, 54, 1663 (1932).

[2] Johnson, Morey and Kott, *ibid.*, 54, 4278 (1932).

Anal. Calcd. for $C_2H_5GeI_3$: I, 78.93; Ge, 15.05. Found: I, 78.97, 79.02. Ge, 15.11, 15.16.

The yield of 23.5 g. of the triiodide corresponds to 86% of the germanous iodide. Since the germanous iodide was known to be somewhat impure due to exposure to air the yield was considered satisfactory.

Properties.—Ethylgermanium triiodide is a mobile lemon-yellow colored liquid. The color, however, deepens as the material is heated, becoming deep red at temperatures about 250°. The triiodide boils at a temperature of 281° under a pressure of 755 mm. while the melting point is between −1.5 and −2.5°. The triiodide dissolves in ordinary organic solvents without apparent change. It is ammonolyzed completely when treated with liquid ammonia, yielding an insoluble white solid, while when treated with water the triiodide dissolves with partial hydrolysis. Ethylgermanium triiodide is relatively stable toward thermal decomposition and may be heated to a temperature of 300° without appreciable change. In this respect its behavior is in marked contrast to that of germano-iodoform which is reported to decompose at room temperature, yielding germanous iodide and hydrogen iodide.[3] Attempts to decompose ethylgermanium triiodide analogously failed. When heated above 350° decomposition takes place with the formation of gas and germanium tetraiodide. While the triiodide does not react appreciably with "molecular" silver at temperatures as high as 220°, it reacts slowly with hot mercury and rapidly with other more electropositive metals at temperatures as low as 100°. Ethylgermanium triiodide is somewhat more stable toward oxidation than might be expected and may be distilled in dry air without change; however, when exposed to air containing traces of moisture marked decomposition occurs.

Monoethylgermanic Oxide $(C_2H_5GeO)_2O$.—When an aqueous solution of ethylgermanium triiodide is boiled with freshly prepared silver oxide, the hot solution filtered and the filtrate concentrated by evaporation, a transparent "cellophane-like" material forms on the surface of the hot solution. On removal of this material from the surface, the surface is soon covered with another solid film. A sample of this "glassy" material which had been dried in an air-bath at a temperature of 110° for one to two hours was shown by analysis to be monoethylgermanic oxide, $(C_2H_5GeO)_2O$.

Anal. Calcd. for $(C_2H_5GeO)_2O$: Ge, 57.78; C, 19.10; H, 4.01. Found: Ge, 57.83, 57.89, 57.82; C, 19.13, 18.99; H, 4.00, 3.93.

The residue obtained by evaporation of the remainder of the solution from which the sample of solid film was obtained, was also found to be monoethylgermanic oxide. Although this method of obtaining the ethylgermanic oxide is conveniently simple, the yields of the germanium compound were always low. Usually not more than 50% of the germanium was obtained as monoethylgermanic oxide.

A more satisfactory method of obtaining ethylgermanic oxide consists in ammonolyzing ethylgermanium triiodide with liquid ammonia, washing the insoluble white ammonolytic product, first with liquid ammonia and finally with cold water. When the washings are found to be iodide-free, the residual solid is dissolved in boiling water, the solution filtered and evaporated. The yields obtained by this method were usually

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(3) Dennis and Judy, THIS JOURNAL, 51, 2326 (1929).

almost quantitative. Of course prolonged washing of the ammonolytic product with water dissolves some of the material, thereby lowering the yield.

Vapor pressure measurements carried out in an attempt to detect a hydrated form of $(C_2H_5GeO)_2O$ failed and indicated that the composition of the solid separating from the saturated solution of the oxide at room temperature has an empirical formula corresponding to $(C_2H_5GeO)_2O$.

Properties.—Monoethylgermanic oxide is a white solid which does not melt when heated to a temperature of 300° but when heated to higher temperatures *in vacuo* sublimation and decomposition occur. The oxide is soluble in water and alcohol and insoluble in petroleum ether. When treated with concentrated solutions of the halogen acids the corresponding trihalide is formed in solution and in the case of the trichloride may be extracted with ether.

Ammonolysis of Ethylgermanium Triiodide.—When liquid ammonia was condensed onto ethylgermanium triiodide contained in a suitable reaction tube, reaction occurred immediately yielding a white precipitate insoluble in liquid ammonia. On the addition of sodium to the mixture hydrogen was at once evolved. When an excess of sodium had been added the hydrogen collected was equivalent to the iodine of the triiodide, showing that the iodide was ammonolyzed. The sodium reacted only with the ammonium iodide formed and not with the ammonolytic germanium product. In order to determine the nature of the germanium compound formed in the reaction, the number of moles of ammonia entering into reaction with one mole of ethylgermanium triiodide was determined. The procedure consisted in condensing liquid ammonia onto a weighed sample of triiodide in a suitable reaction tube of known weight, agitating the mixture thoroughly, removing the excess ammonia by means of a vacuum pump, and reweighing the reaction tube. From the gain in weight of the reaction tube the number of moles of ammonia entering into reaction with the triiodide is at once obtained. In some cases the reaction tube was exhausted to about 0.01 mm. at −33° as quickly as possible, while in others the tube was evacuated at room temperatures during many hours. In all cases the gain in weight of the reaction tube corresponded to about 4.17 moles of ammonia per mole of the triiodide. However, when the reaction product in the closed tube was heated to a temperature of 150° during half an hour ammonia was evolved. The tube and its contents were cooled to room temperature, the tube opened and the liberated ammonia removed by means of a vacuum pump. The weight of the reaction tube after heating indicated that four moles of ammonia had entered into reaction with the triiodide. The over-all reaction is thus $C_2H_5GeI_3 + 4NH_3 = C_2H_5GeN + 3NH_4I$, while either a complex intermediate reaction or an unusual adsorption phenomenon occurs. As a check on these results water was condensed into the reaction tube and the mixture allowed to stand for several hours. Finally, the excess water as well as the ammonia liberated by hydrolysis of the nitride was removed from the reaction mixture by means

TABLE I

AMMONOLYSIS OF ETHYLGERMANIUM TRIIODIDE

Expt.	$C_2H_5GeI_3$, g.	NH_3[1], g.		Mole NH_3[a] mole $C_2H_5GeI_3$		H_2O-NH_3[b]	
		a	b	a	b	Calcd.	Obs.
1	1.3374	0.1972	...	4.177	...	...	...
2	0.4541	.0667	...	4.161	...	...	...
3	1.1327	.1665	0.1599	4.164	3.999	0.0235	0.0250
4	1.0740	.1576	.1511	4.170	3.999	.0222	.0231

[a] The weight of NH_3 in column a is the weight of ammonia before heating the tube, while in column b the weights are those obtained after the heating process. The mole ratios are based on these weights.

[b] The values are calculated from equation 3 and the original weight of sample.

of a vacuum pump and the reaction tube reweighed. The results of these experiments were consistent with the previous observations and indicated that the nitride hydrolyzed as anticipated, according to the equation $2C_2H_5GeN + 3H_2O = (C_2H_5GeO)_2O + 2NH_3$. The results are recorded in the table.

The ammonolysis of ethylgermanium tribromide was also studied and confirmed the above results, four moles of ammonia per mole of tribromide being obtained for the over-all reaction, while for the intermediate reaction an average of 4.17 was found.

Ethylgermanium Tribromide, Trichloride and Trifluoride.—The three halides were prepared by passing the dry hydrogen halide over a mixture of phosphorus pentoxide and ethylgermanic oxide. The liquid products were purified by fractional distillation *in vacuo* and the pure trihalide kept in sealed fragile bulbs. The tribromide was analyzed for germanium and bromine, and the trichloride for chlorine, while the trifluoride was identified by vapor density determinations together with a semi-quantitative determination of the fluorine content wherein the fluorine was weighed as lead chlorofluoride.

Anal. Calcd. for $C_2H_5GeBr_3$: Br, 70.23; Ge, 21.27. Found: Br, 70.18, 70.20; Ge, 21.38, 21.58. Calcd. for $C_2H_5GeCl_3$: Cl, 51.14. Found: Cl, 50.96, 50.89. Calcd. for $C_2H_5GeF_3$: F, 35.9; mol. wt., 158.5. Found: F, 36.5; mol. wt. (vap. density), 159.5.

Properties of Ethylgermanium Trihalide.—These three halides are colorless mobile liquids which fume in air. The boiling points of the tribromide, trichloride and trifluoride are, respectively, 200° (763 mm.), 144° (762 mm.), and 112° (750 mm.). Ethylgermanium trifluoride melts between −15.5 and −16.5° while neither the tribromide nor the trichloride freeze when cooled in a bath of liquid ammonia boiling at atmospheric pressure. Like the triiodide the hydrolysis of these halides is homogeneous, and they are ammonolyzed when treated with liquid ammonia and soluble in common organic solvents.

Summary

Ethylgermanium triiodide was prepared by the action of ethyl iodide on germanous iodide. From the ammonolysis of ethylgermanium triiodide monoethylgermanium nitride was obtained. Hydrolysis of the nitride gave monoethylgermanic oxide. From the reaction of monoethylgermanium oxide and halogen halides, ethylgermanium trihalides were prepared.

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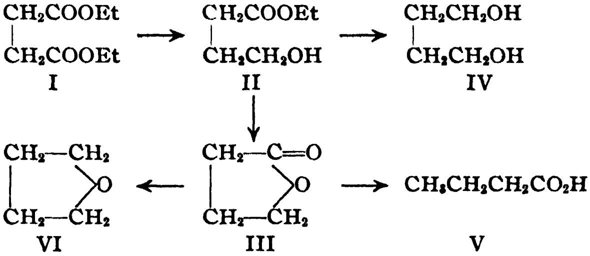
Hydrogenolysis of Succinates and Glutarates

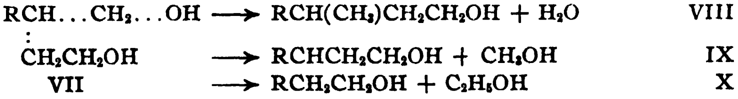
BY BRUNO WOJCIK AND HOMER ADKINS

The marked labilizing effect of carbinol and carbethoxy groups in the 3 position upon the cleavage of carbon to oxygen linkages has been observed in the hydrogenolysis of trimethylene glycol, ethyl β-hydroxybutyrate, malonic ester, etc., to the corresponding monohydric alcohols.[1] The effect of an oxygenated substituent in the 4 or 5 position is less marked than in the 3 position, but may be of considerable importance from a preparational standpoint. In order to illuminate this situation, a study has been made of the hydrogenolysis of various substituted succinates and glutarates.

The hydrogenolysis of diethyl succinate I results in the formation of ethyl γ-hydroxybutyrate II, butyrolactone III, tetramethylene glycol IV, butyric acid V and probably of tetrahydrofuran VI.



Cleavage in a substituted succinate may also occur at one of the O to C or at either of two of the C to C linkages as in VIII to X.[2]



$$\begin{array}{llr} \text{RCH}\ldots\text{CH}_2\ldots\text{OH} & \longrightarrow \text{RCH(CH}_3\text{)CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} & \text{VIII} \\ \vdots & & \\ \text{CH}_2\text{CH}_2\text{OH} & \longrightarrow \text{RCHCH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{OH} & \text{IX} \\ \quad\text{VII} & \longrightarrow \text{RCH}_2\text{CH}_2\text{OH} + \text{C}_2\text{H}_5\text{OH} & \text{X} \end{array}$$

Fortunately, the major products obtained from a given succinate under the optimum conditions are few in number, as will be evident from the summary of the effect of experimental conditions and structure upon the type and ratio of products.

The successful preparation of tetramethylene glycol from diethyl succinate demands that the reaction be carried out rapidly. Such a rapid hydrogenolysis occurred when 523 g. of pure ester and hydrogen under a pressure of 300 atm. were allowed to react at 250° over 30 g. of copper-chromium oxide. The reaction was almost complete after one hour and

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(1) Connor and Adkins, THIS JOURNAL, 54, 4678 (1932).

(2) It is not known whether it is the ester or the glycol which suffers C to C cleavage. For convenience the cleavage will be represented as occurring to the glycol. The labile linkages are represented by dotted lines in the formulas.

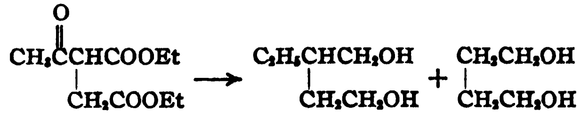
entirely so after two hours. The yield of glycol (200 g.) was 74% of the theoretical accompanied by 44 g. of butyrolactone. Lower pressure of hydrogen or ratio of catalyst to ester resulted in decreasing the yield of glycol because of the deleterious effect of acid and water, formed during the hydrogenolysis, upon the activity of the catalyst. The more rapid the reaction, the lower the concentration of these products and the shorter the period during which the catalyst may deteriorate.

The chief product obtained from succinic anhydride was butyrolactone (31%) while butyric and succinic acids were also formed. It is probable but not certain that tetrahydrofuran was also among the products of reaction. The catalyst does not have a long life in the presence of water, anhydrides and acids, so that it is difficult to obtain complete reaction of the anhydride.

A hydrogenolysis of diethyl α-methylsuccinate under conditions similar to those used for diethyl succinate also gave a good yield (72%) of the corresponding 2-methylbutanediol-1,4. But under milder conditions, fifteen hours and two applications of catalyst were necessary since it was reduced to the red or inactive form. No glycol was obtained in this latter run but the reaction proceeded to give alcohols corresponding to VIII, IX and X in which R is methyl. Similarly, when diethyl α-isopropylsuccinate was submitted to hydrogenolysis at 300 atmospheres a 30% yield of the corresponding glycol (R is isopropyl in VII) was obtained while the chief product (70%) of a slower hydrogenolysis was isohexyl alcohol corresponding to IX, accompanied by 3,4-dimethylpentanol-1 as in VIII.

The strong influence of a phenyl group in the β position to a hydroxyl in labilizing the carbon to oxygen linkage[3] toward hydrogenolysis has so far rendered futile all attempts to prepare 2-phenylbutanediol-1,4 in yields above 13 to 23% from diethyl α-phenylsuccinate. The chief product (70 to 80%) was 3-phenylbutanol-1 as in VIII, while IX and X occurred to a very small extent, if at all.

In addition to the possibilities indicated in I to X, two glycols were produced from acetyl succinate depending upon whether the acetyl group was eliminated as ethanol by hydrogenolysis or was hydrogenated to an ethyl group. Due to the similarity of their boiling points the glycols were not separated.



$$\begin{array}{l} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CHCOOEt \\ \quad | \\ \quad CH_2COOEt \end{array} \longrightarrow \begin{array}{l} C_2H_5CHCH_2OH \\ \quad | \\ \quad CH_2CH_2OH \end{array} + \begin{array}{l} CH_2CH_2OH \\ | \\ CH_2CH_2OH \end{array} \qquad XI$$

Analysis of the mixture for carbon and hydrogen and the acetyl values indicated that the two glycols were present in similar amounts. A considerable yield of a butyrolactone (29%) was also obtained, but it has not been

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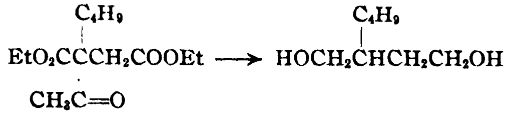
(3) Adkins, Wojcik and Covert, THIS JOURNAL, 55, 1699 (1933).

established as to whether this compound is an α or β ethyl or an α-β dimethyl butyrolactone.[4]

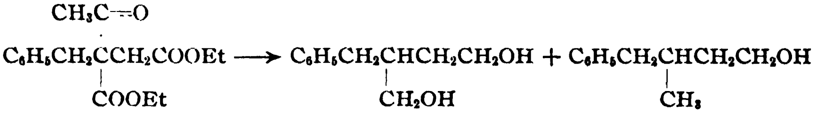
A disubstituted succinate, diethyl α-*n*-butyl α-acetyl succinate, underwent a smooth and rapid hydrogenolysis to give a 79% yield of 2-*n*-butylbutanediol-1,4.



$$EtO_2C\underset{\substack{|\\ CH_3C=O}}{\overset{\substack{C_4H_9\\ |}}{C}}CH_2COOEt \longrightarrow HOCH_2\overset{\substack{C_4H_9\\ |}}{C}HCH_2CH_2OH \qquad XII$$

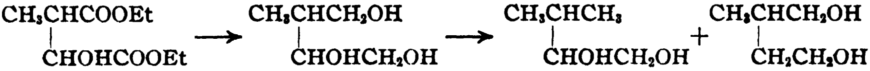
The complete removal of the acetyl group in reaction XII as contrasted with its partial removal in XI is understandable if it is noted that the butylacetylsuccinate is a disubstituted β-keto ester. Such compounds are quantitatively cleaved by hydrogen at the linkage between the carbonyl and the tetrasubstituted carbon atom.[1]

Another disubstituted succinate, diethyl α-benzyl-α-acetyl-succinate, underwent a similar cleavage to give 2-benzylbutanediol-1,4, but the yield was low (35%) and an equal amount of 3-benzylbutanol-1 was formed. This latter product is the result of the cleavage (under the influence of phenyl) of a C to O linkage as in VIII.



$$C_6H_5CH_2\underset{\substack{|\\ COOEt}}{\overset{\substack{CH_3C=O\\ |}}{C}}CH_2COOEt \longrightarrow C_6H_5CH_2\underset{\substack{|\\ CH_2OH}}{C}HCH_2CH_2OH + C_6H_5CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2OH \qquad XIII$$

The hydrogenolysis of diethyl α-methyl-β-hydroxysuccinate (XIV) resulted in the formation of two isomeric glycols, 3-methylbutanediol-1,2 (XVI), and 2-methylbutanediol 1-4 (XVII).



$$\begin{matrix} CH_3CHCOOEt \\ | \\ CHOHCOOEt \end{matrix} \longrightarrow \begin{matrix} CH_3CHCH_2OH \\ | \\ CHOHCH_2OH \end{matrix} \longrightarrow \begin{matrix} CH_3CHCH_3 \\ | \\ CHOHCH_2OH \end{matrix} + \begin{matrix} CH_3CHCH_2OH \\ | \\ CH_2CH_2OH \end{matrix}$$

XIV XV XVI XVII

The ratio of products was determined by the relative rates of cleavage of the two β-hydroxyl groups in the triol XV, each of which was labilizing the other. The difference between the sum of the yields of glycols (74%) and the theoretical is no doubt accounted for by the cleavage of carbon to carbon linkages as in VIII, IX and X.

The hydrogenation to the glycols of the ethyl esters of unsubstituted acids above succinic presents no difficulties. Pentamethylene, hexamethylene, decamethylene and tetradecamethylene glycols have been prepared in yields above 95% from the esters of the corresponding acids. Even the substitution of a phenyl group on the middle carbon of diethyl glutarate did not have much effect as an 89% yield of $C_6H_5CH(CH_2CH_2OH)_2$ was obtained. An acetyl group on an α carbon of glutaric ester has the same effect as in a succinate, that is, two glycols are produced in about equal amounts, each of which contains one more methylene group than the glycols from the succinate in XI. In contrast with this is the behavior of a disubstituted acetoacetic ester, α-acetyl-α-ethyladipic ester, which upon hydrogenation gave a single glycol 2-ethyl-hexanediol-1,6, the acetyl group in the ester having been completely removed by hydrogenolysis.

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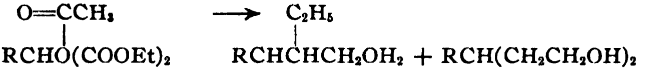
[4] Glycols and alcohols containing the group CH_3CHOH— are possible products from the hydrogenolysis of α-acetyl succinates, glutarates, etc. However, tests by the haloform reaction showed that such alcohols and glycols were not present in the reaction products referred to in this paper.

The α,γ-diacetyl-β-methyl-(or phenyl)-glutarates (XVIII) may be regarded as monosubstituted acetoacetic esters and so might give the two types of cleavage. The C to C cleavage appears to occur only to a slight extent, the main product being 3-methyl-(or phenyl)-2,4-diethyl pentanediol-1,5 resulting from the hydrogenation of the acetyl groups. Connor[1] first observed this reaction and upon the basis of the high yields



$$\underset{\text{XVIII}}{\mathrm{RCH\overset{\overset{\displaystyle O{=}CCH_3}{|}}{C}(COOEt)_2}} \longrightarrow \underset{\text{XIX}}{\mathrm{RCH\overset{\overset{\displaystyle C_2H_5}{|}}{C}HCH_2OH_2}} + \underset{\text{XX}}{\mathrm{RCH(CH_2CH_2OH)_2}}$$

obtained, and the analysis of the glycols for carbon and hydrogen, it was concluded that the acetyl group had not been split off. The high yields (96 or 97%) of glycols are significant in this connection because if the ethyl groups were not present in the glycols, the yields obtained would be considerably over 100%. However, the analysis for carbon and hydrogen was always somewhat low for the indicated compounds. His experiments were repeated several times, and an intermediate dihydroxy ester prepared and submitted to hydrogenolysis. The results were always the same, *i. e.*, excellent yields of a glycol which analyzed low in carbon and hydrogen. These low analyses are probably due to the presence of a small amount of glycol XX which could not be removed from the two racemic mixtures of glycol XIX by fractionation.

Finally four dicarbethoxyglutarates XXI, where R is H, CH_3, C_3H_7 or C_6H_5 (prepared by the condensation of formaldehyde, acetaldehyde,

$$\underset{\text{XXI}}{\mathrm{RCH(CH(COOEt)_2)_2}} \longrightarrow \underset{\text{XXII}}{\mathrm{RCH(CH_2CH_2OH)_2}} + \underset{\text{XXIII}}{\mathrm{RCH(CH(CH_3)CH_2OH)_2}} + \underset{\text{XXIV}}{\mathrm{R(CH_2)_3OH}}$$

butyraldehyde or benzaldehyde with malonic ester) were submitted to hydrogenolysis. These compounds, which may be regarded as monosubstituted malonic esters, behave as do the simpler monosubstituted malonic esters. That is, the main reaction is the elimination of one of each of the carbethoxy groups of the malonic ester residues with the formation of a glycol XXII. The yield of glycol from three of the esters was 70 to 91%. A small yield (1%) of a solid glycol of type XXIII was obtained when R is phenyl. The β-phenyl and β-propyl dicarbethoxyglutarates in addition to the glycols gave 27 to 30% yields of 3-phenylpropanol-1 and hexanol-1, respectively, by cleavage between the α and β carbons as in XXIV.

The experimental results are summarized in the tables.

TABLE I

EXPERIMENTAL RESULTS[a]

Esters diethyl	Boiling pt. °C.	Mm.	G.	Time, hrs.	Products G.	
α-Methylsuccinate[6]	98–99	10	228	1	9	Isoamyl alcohol, 127–129°
					90	2-Methylbutanediol-1,4 126–127° (14 mm.)[13]
α-Methylsuccinate	98–99	10	115	0.7[h]	11	α-Methylbutyrolactone (84–86° (12 mm.)
					40	Diol
α-Isopropylsuccinate[6]	112–114	9	22	3[b]	2.4	Alcohols, 103–138°
					7.9	Isohexyl alcohol 146–151°[14]
α-Isopropylsuccinate	112–114	9	100	6.5	7.3	Alcohols, 123–137°
					8.1	Isohexyl alcohol
					3.2	3,4-Dimethylpentanol-1, 159–162°
					11 8	Unchanged ester
					16.4	2-Isopropylbutanediol-1,4 (119–122°) (3 mm.)
α-Butyl-α-acetylsuccinate[7]	136–138	4	75	1	37.4	2-*n*-Butylbutanediol-1,4, 135–137° (3 mm.)
α-Benzyl-α-acetylsuccinate[7, 15]	165–167	4	40	1	8.4	3-Benzylbutanol-1, 103–107° (3 mm.)
					8.1	2-Benzylbutanediol-1,4, 162–165° (3 mm.)
α,γ-Dicarbethoxyglutarate[8]	193–195	14	166	5	47.2	Pentanediol-1,5, 229–231°[c]
β-Methyl-α,γ-dicarbethoxyglutarate[9]	185–190	6	65	10	18 2	3-Methylpentanediol-1,5, 134–137° (6 mm.)[d]
β-Phenyl-α,γ-dicarbethoxyglutarate[20]	184–186	3	153	7.5	13.8	3-Phenylpropanol-1, 105–107° (5 mm.)
					47.6	3-Phenylpentanediol-1,5, 174–176° (5 mm.)
					1.1	2,4 - Dimethylphenylpentanediol - 1,5, m. p., 115–116°
β-Propyl-α,γ-dicarbethoxyglutarate[9]			40	2	14.2	Alcohols and water, 76–79°
					3.7	*n*-Hexyl alcohol, 146–150°
					8.7	3-Propylpentanediol-1,5, 134–136° (10 mm.)
α,γ-Diacetyl-β-phenylglutarate[10,11]	M151–152		79	8	49	2,4 - Diethyl - 3 - phenylpentanediol - 1,5, 174–179° (2–3 mm.)
Dodecamethylenedicarboxylate[12,e]			202	4	141	Tetradecanediol-1,14, m. p. 85°[e]
α-Keto-β-methylsuccinate[f]	144–146	21	202	14	184	Diethyl α-hydroxy-β-methylsuccinate, 109–113° (5 mm.)
α-Hydroxy-β-methylsuccinate[18]	109–113	5	102	10	53.5	Alcohols and water, 75–88°
					19.3	3-Methylbutanediol-1,2, 81–83° (5 mm.)[13,17]
					13.2	2-Methylbutanediol-1,4, 105–107° (7 mm.)[j]
α-Acetyl-α-ethyladipate[7]			46	3	2.6	Alcohols, 45–90° (4 mm.)
					18.1	2-Ethylpentanediol-1,5
α,γ-Diacetyl-β-phenylglutarate[10,11]	M151–152		35	[g]	34.1	3,5 - Dicarbethoxy - 4 - phenylheptanediol-2,6, m. p. 162–163°
α-Phenylsuccinate[h]	153–155	6	38	3	16.2	3-Phenylbutanol-1, 110–111° (6 mm.)
					3.2	2-Phenylbutanediol-1,4, 162–165° (7 mm.)
α-Acetylsuccinate[7]	142–144	16	144	2	40.2	Alcohols and water, 70–86°
					21.2	A lactone[i] $C_6H_{10}O_2$, 85–87° (5 mm.)[16]
					38.9	Glycols, 113–114° (5 mm.)
β-Phenylglutarate			35	1.5	21.2	3-Phenylpentanediol-1,5, 190–192° (14 mm.)[l]
α-Acetylglutarate	150–153	16	139	11.5	48.3	2-Ethylpentanediol-1,5 and pentanediol-1,5, both 129–130° (7 mm.)[k,19]
Succinic anhydride	M118–119		100	24	28.9	Butyrolactone, 196–200°[m]

[a] Unless specified otherwise, the reactions were at 250° under 200 to 300 atmospheres pressure of hydrogen with approximately 1 part of copper–chromium oxide for 10 parts of ester. [b] 100 atmospheres. [c] The saponification value of the diacetate was 7 to 8 units high indicating the presence of a little of the 2,4-dimethylpentanediol-1,5. [d] The glycol contained enough of the 2,4-dimethyl compound to make the saponification equivalent 12 to 14 units high (see table). [e] The ester was prepared and the glycol isolated by Dr. E. Prill. [f] In 300 ml. of EtOH at 200°. [g] Reaction was complete by the time the temperature reached 150°. [h] At 150 atm. (Covert obtained yields of the glycol as high as 23% by interrupting the hydrogenation when 75% of the ester had reacted with hydrogen). [i] Saponification value for the lactone $C_6H_{10}O_2$: found 113, calcd. 114. [j] Both glycols were identified by saponification values of their acetates and by comparison with physical constants previously described.[11] [k] Two applications of catalyst. [l] 150 atm., 50 ml. of EtOH as solvent. [m] There was a considerable amount of very volatile material, tetrahydrofuran (?), butyric acid, succinic acid and water.

TABLE II

ANALYTICAL DATA

Name of compound	Mol. formula	n^{25}_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. weight of acetate Calcd.	Mol. weight of acetate Found
3,4-Dimethylpentanol-1	$C_7H_{16}O$	1.4261	72.41	72.27	13.79	13.34	158	161
2-Isopropylbutanediol-1,4	$C_7H_{16}O_2$	1.4535	63.63	63.53	12.12	12.04	...	...
2-*n*-Butylbutanediol-1,4	$C_8H_{18}O_2$	1.4530	65.75	65.66	12.32	12.11	230	234
2-Ethylbutanediol-1,4	$C_8H_{18}O_2$	1.4568	65.75	65.65	12.32	12.29	...	...
Diethyl α-ethyl α-acetyl adipate	$C_{14}H_{24}O_5$	1.4445	61.76	61.63	8.82	8.81	...	...
2-Benzylbutanediol-1,4	$C_{11}H_{16}O_2$	1.5210	73.33	73.24	8.88	9.20	...	...
4-Phenyl-3-methylbutanol-1	$C_{11}H_{16}O$	1.5078	80.48	80.13	9.75	9.70	206	211
3-*n*-Propylpentanediol-1,5	$C_8H_{18}O_2$	1.4569	65.75	66.14	12.32	12.19	...	...
3-Phenyl-2,4-dimethylpentanediol-1,5	$C_{13}H_{20}O_2$	[a]	75.00	74.63	9.61	9.39	...	...
3-Methylpentanediol-1,5	$C_6H_{14}O_2$	1.4512	61.01	61.94	11.86	11.74	202	214
3-Phenyl-2,4-diethylpentanediol-1,5	$C_{15}H_{24}O_2$	[a]	76.27	75.59	10.17	9.45	...	...
3-Methyl-2,4 diethylpentanediol-1,5	$C_{10}H_{22}O_2$	[a]	69.00	67.5	12.64	10.7	...	...
4-Phenyl-3,5-dicarbethoxy heptanediol-2,6	$C_{19}H_{28}O_6$	....	64.77	64.73	7.95	7.67	...	..
Diacetate of 2,4-diethyl-3-phenylpentanediol-1,5	$C_{19}H_{28}O_4$	....	71.25	71.85	8.75	8.40	...	.
Diethyl α-acetyl α-*n*-butylsuccinate	$C_{14}H_{24}O_5$	1.4335	61.76	61.67	8.82	8.99	...	...

[a] This product as indicated in the discussion was probably not homogeneous.

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(5) Bruhl, *Ber.*, **26**, 338 (1893).

(6) Kachler, *Ann.*, **169**, 172 (1873).

(7) Isbell, Wojcik and Adkins, THIS JOURNAL, **54**, 3684 (1932).

(8) Welch, *J. Chem. Soc.*, 673 (1931).

(9) Kotz and Stalmann, *J. prakt. Chem.*, [2] **68**, 157 (1903).

(10) Hantzsch, *Ber.*, **18**, 2583 (1885).

(11) Knoevenagel, *Ann.*, **281**, 75 (1894).

(12) Chuit, *Helv. Chim. Acta*, **9**, 272 (1926).

(13) Faworsky, *Ann.*, **354**, 383 (1907).

(14) Rossi, *ibid.*, **133**, 180 (1865).

(15) Conrad, *Ber.*, **11**, 1058 (1878).

(16) Chauloroff, *Ann.*, **226**, 338 (1884); Fichter and Busswenger, *Ber.*, **36**, 1204 (1903).

(17) Wagner, *ibid.*, **21**, 1232 (1888).

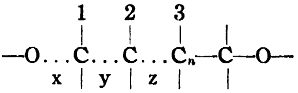
(18) Wislicenus, *ibid.*, **25**, 202 (1892).

(19) Manske, THIS JOURNAL, **53**, 1109 (1931).

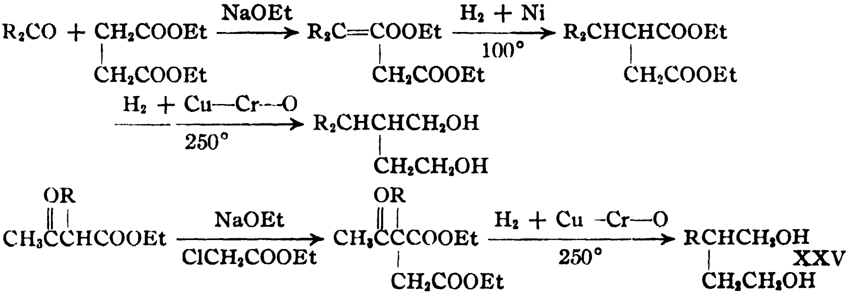
(20) Kotz, *J. prakt. Chem.*, [2] **75**, 488 (1907).

Conclusions

The system under study may be represented as shown, where the dotted lines indicate the labile linkages, x, y, z. The effect of substitution upon readiness of hydrogenolysis may be stated as follows: a phenyl or benzyl group at 1 or 2 weakens the x linkage. A methyl group at 2 has little labilizing effect while a branched chain (isopropyl) at 2 weakens y, and to a less extent x. An oxygenated substituent $\left(\text{—COOEt or } CH_2OH,\ CH_3\overset{O}{\overset{\|}{C}}\text{— or } CH_3CHOH\text{—}\right)$ at 2 weakens x and y equally. Methyl at 1 with —COOEt (or CH_2OH) at 2 facilitates cleavage at x. An alkyl or aryl group at 3 with an oxygenated substituent at 2 weakens z. With both an alkyl and an oxygenated substituent at 2, y is cleaved almost quantitatively. An increase in *n* stabilizes y and z.



The reactions described above make it feasible to prepare 2-alkylbutanediols-1,4 by means of two series of reactions



$$R_2CO + \underset{CH_2COOEt}{CH_2COOEt} \xrightarrow{NaOEt} \underset{CH_2COOEt}{R_2C{=}COOEt} \xrightarrow[100^\circ]{H_2 + Ni} \underset{CH_2COOEt}{R_2CHCHCOOEt}$$

$$\xrightarrow[250^\circ]{H_2 + Cu{-}Cr{-}O} \underset{CH_2CH_2OH}{R_2CHCHCH_2OH}$$

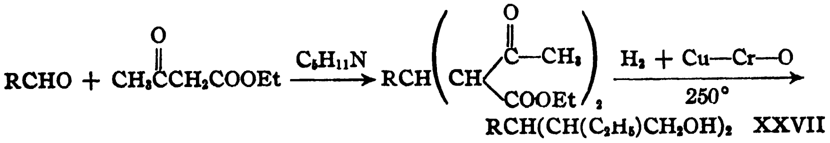
$$CH_3\overset{O}{\overset{\|}{C}}\overset{R}{\overset{|}{C}}HCOOEt \xrightarrow[ClCH_2COOEt]{NaOEt} \underset{CH_2COOEt}{CH_3\overset{O}{\overset{\|}{C}}\overset{R}{\overset{|}{C}}COOEt} \xrightarrow[250^\circ]{H_2 + Cu{-}Cr{-}O} \underset{CH_2CH_2OH}{RCHCH_2OH} \quad XXV$$

A 2-alkylpentanediol-1,5 may be prepared by the method (XXV) above by substituting β-chloropropionic ester for α-chloroacetic ester. A fairly pure 3-alkyl-(or aryl)-pentanediol-1,5 may be made by the series of reactions

$$RCHO + CH_2(COOEt)_2 \xrightarrow[\text{or } NaOEt]{C_5H_{11}N} RCH(CH(COOEt)_2)_2 \xrightarrow[250^\circ]{H_2 + Cu{-}Cr{-}O}$$

$$RCH(CH_2CH_2OH)_2 \quad XXVI$$

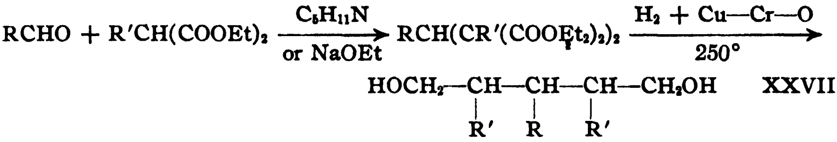
or a 3-alkyl-(or aryl)-2,4-diethylpentanediol-1,5 by the reactions



$$RCHO + CH_3\overset{O}{\overset{\|}{C}}CH_2COOEt \xrightarrow{C_5H_{11}N} RCH\left(CH\left\langle\begin{array}{l}\overset{O}{\overset{\|}{C}}{-}CH_3\\ COOEt\end{array}\right.\right)_2 \xrightarrow[250^\circ]{H_2 + Cu{-}Cr{-}O}$$

$$RCH(CH(C_2H_5)CH_2OH)_2 \quad XXVII$$

However, the best way to prepare a pure 2,4-dialkylpentanediol-1,5 would be through the use of a monosubstituted acetoacetic or malonic ester having the proper substituent, for example



$$RCHO + R'CH(COOEt)_2 \xrightarrow[\text{or NaOEt}]{C_5H_{11}N} RCH(CR'(COOEt)_2)_2 \xrightarrow[250°]{H_2 + Cu—Cr—O} HOCH_2—\underset{R'}{CH}—\underset{R}{CH}—\underset{R'}{CH}—CH_2OH$$

XXVIII

Summary[21]

A number of ethyl esters of dibasic acids containing four or more carbons, variously substituted, have been subjected to the action of hydrogen at 100 to 300 atmospheres at 250° over copper-chromium oxide. The isolation of the major products from these reactions has led to certain conclusions with regard to the relation of structure to susceptibility to cleavage of C to C and C to O linkages, and with regard to feasible methods for preparing various glycols and alcohols.

[21] I wish to record here my indebtedness to Charles Sumner Slichter who, as Dean of the Graduate School and Chairman of the University Research Committee, has for thirteen years unwaveringly supported me through the allotment of funds for the purchase of important apparatus and for the employment at various times of B. H. Nissen, W. A. Lazier, A. E. Broderick, Howard Cramer, Karl Folkers, Ralph Connor and Bruno Wojcik as research assistants.

MADISON, WISCONSIN RECEIVED JULY 31, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 96]

The Rates of the Thermal Decomposition of Certain Triphenylmethyl Alkyl Ethers[1]

BY JAMES F. NORRIS AND ARTHUR CRESSWELL

It has been shown[2] that ethers of the type $(C_6H_5)_3C—O—R$, in which R represents an alkyl radical, decompose under the influence of heat into triphenylmethane and a product formed from the alkoxyl group as the result of the loss of one hydrogen atom; in the case of the ethyl ether acetaldehyde is formed. The temperature at which pyrolysis begins to be evident is definite when an ether of this type is heated in such a way that the temperature is raised at a fixed rate. Under the same conditions the several ethers decompose at different temperatures.

Since pyrolysis takes place in a relatively simple way and the primary products are stable under the conditions used, it seemed probable that the study of the rates at which typical ethers of this structure undergo pyrolysis would yield information of value. The methyl, ethyl and isopropyl ethers derived from triphenylcarbinol were studied with the expectation that something would be learned in regard to the order of the decompositions, their temperature coefficients and the effect on the rate of the temperature interval between the temperature at which pyrolysis begins and that at which the pyrolysis is effected.

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[1] From a part of the thesis presented by Arthur Cresswell in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1932.

[2] Norris and Young, THIS JOURNAL, 52, 753 (1930).

It was found in the case of the ethyl ether that up to about 11% decomposition the velocity constant was of the first order—at 259° $K = 0.010$, at 269° $K = 0.021$. The rate of decomposition doubled approximately for a rise of 10°. Beyond this point the calculated velocity constant increased with the time.

The isopropyl ether showed the characteristics of a monomolecular reaction up to about 28% decomposition. The first order velocity constants were as follows: at 259° 0.016, at 270° 0.032, at 289° 0.080.

At 259° the first order constant for the ethyl ether was 0.010 and for isopropyl ether 0.014. This temperature is 17° above the cracking temperature[3] of the ethyl ether (242°) and 39° above that of the isopropyl ether (220°). At 270, 28 and 50 degrees, respectively, above the cracking temperatures, the constants were 0.021 and 0.028. It appears that the rates of decomposition of the two similar ethers are approximately equal at the same temperatures, although these temperatures bear a different relationship to the cracking temperatures of the two compounds.

At 270° the rates of pyrolysis increased with time after the ether had been heated for five hours. Since the increase in rate with time at a constant temperature was particularly marked in the case of the methyl ether, which showed this behavior at the lower temperatures, this ether was studied more fully in order to discover the cause of this behavior.

The rates of decomposition of the methyl ether (cracking temperature 262°) were determined at 268, 277, 280 and 298°. In all cases the rate increased with time.

Large scale complete decompositions of the methyl and the ethyl ethers were made to determine the products of decomposition so that the effect of the latter on the rate could be investigated. Previous work had shown that the chief products of the decomposition of all the ethers of this type are triphenylmethane and an aldehyde when the radical is a primary one and a ketone when it is secondary.

The ethyl ether yielded the expected products and a small amount of carbon monoxide, which indicated that about 4% of the ester had decomposed in a way to give this gas. The methyl ether gave carbon monoxide and methyl alcohol in addition to triphenylmethane and formaldehyde. It appears from these results that the methoxyl group can yield products which result from at least two modes of decomposition

$$CH_3O\text{—} = CH_2O + (H)$$
$$2CH_3O\text{—} = CH_3OH + CO + 2(H)$$

The hydrogen atoms are used up in the formation of triphenylmethane.

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[3] The cracking temperatures given are the temperatures at which the ethers first show signs of decomposition when the temperatures at which they are heated are raised at the rate of one degree per minute.

About 40% of the methyl ether produced in its decomposition methyl alcohol and carbon monoxide. This difference between methyl and ethyl ethers is shown in the case of other compounds which are not being studied.

In order to determine whether the products of the pyrolysis of the methyl ether had an effect on the rate of its decomposition the rates were determined in the presence of triphenylmethane, methyl alcohol and formaldehyde. When a mixture of the ether and hydrocarbon in the molecular ratio of 2 of the former to 1 of the latter was pyrolyzed at 268° the decomposition at the end of two hours was twice that of the ether alone; at the end of five hours 1.3 times as great. At 280° at the end of two hours the rate was 3.6 and of five hours 2.2 times as great. The greater effect at the beginning of the decomposition is what would be expected. In the presence of methyl alcohol the pyrolysis was slightly retarded. With formaldehyde the results were not conclusive.

The Effect of the Presence of Oxygen on the Rate of Pyrolysis.—All the results stated above were obtained when the ethers were pyrolyzed in the presence of a small volume of air. The tubes used were of such a size that the volume of the air present was approximately 5 cc. In order to determine whether the oxygen present affected the rate of cracking, parallel experiments were carried out with the methyl ether at the same time in the presence of and in the absence of air. In the latter case the tubes containing the ether were evacuated and filled with nitrogen three times before being sealed. In two experiments at 268° in the presence of air the percentage decomposition at the end of six hours was 12.66 and 12.78; in the presence of nitrogen the percentages were 1.83 and 1.83. The difference found must be due to the catalytic influence of oxygen since the weight of the gas present could produce an almost negligible effect if ordinary oxidation were involved. These results led to a further study in this Laboratory of the effect of the presence of traces of oxygen on rates of pyrolysis and cracking temperatures. This work will be reported later. It has been shown in the case of ethers derived from diphenylcarbinol that the cracking temperatures and rates of decomposition are markedly affected.

Experimental Details

Compounds Used.—The ethers were made by the method of Norris and Young.[2] It was found that triphenylmethyl methyl ether could be distilled without decomposition under diminished pressure; it boiled at 163° (2 mm.), 183° (4 mm.) and 195° (5 mm.). The ether, after crystallization, melted at 82.6–82.9° as reported in the earlier work in which the ether was not distilled. A large sample of the ether, which had this melting point and was prepared in the spring, was found to melt at 95.5–96° in the following autumn. All samples subsequently prepared in the same way melted at the higher point. This behavior of the ether will be further studied. The ethyl and the isopropyl ethers did not show a similar change in melting point. The samples used melted at 81.2–81.8, and 111°, respectively.

Experimental Method.—In determining the rates of pyrolysis, accurately weighed samples of the ether (approximately 0.5 g.) were placed in tubes of glass (internal diameter 10 mm., length 120 mm., drawn out tip 20 mm.) which were sealed. A number of tubes were placed in a thermostat which was electrically heated and controlled, contained a fan, and held the temperature constant with a maximum variation of 0.5°. The tubes were removed at intervals of one hour and examined. A small flame was held in contact with the tip until a small hole was formed. The tube was connected with a vacuum pump, rotated, heated to 100°, cooled and weighed. This procedure was repeated until the weight became constant. Two blank determinations were made in a similar way with tubes which contained triphenylmethane only. The change in weight was not greater than 0.2 mg.

Rates of Pyrolysis.—It will be seen from the table that the calculated first order velocity constants for the methyl ether increase with time. In the cases of the other ethers the increase is noticeable at the higher percentage decompositions.

RATES OF PYROLYSIS OF TRIPHENYLMETHYL ALKYL ETHERS

Methyl Ether

Time, hours	% decomp. at 268°	First order vel. const.	% decomp. at 277°	First order vel. const.	% decomp. at 280°	First order vel. const.	% decomp. at 298°	First order vel. const.
2	1.1	0.005	1.8	0.009	2.9	0.005	3.8	0.019
3	..	...	4.0	.014	6.2	.021	10.9	.038
3.4	3.8	.011	..	...	..	...	..	...
4	..	...	7.7	.020	11.1	.030	29.7	.088
4.1	4.9	.012	..	...	..	...	..	...
5	6.6	.014	10.1	.021	16.5	.037	43.1	.11
6	11.3	.020	15.5	.022	23.9	.047	..	...

Ethyl Ether

Time, hours	% decomp. at 259°	First order vel. const.	% decomp. at 269°	First order vel. const.	% decomp. at 270°	First order vel. const.
2	2.3	0.010	4.1	0.021	4.1	0.021
3	3.0	.010	7.6	.025	6.1	.021
4	3.9	.010	8.4	.021	7.2	.018
5	..	...	10.3	.021	9.2	.018
6	..	...	11.1	.019	13.6	.023
	Average	.010		.021		.020

Isopropyl Ether

Time, hours	% decomp. at 259°	First order vel. const.	% decomp. at 270°	First order vel. const.	% decomp. at 289°	First order vel. const.
1	1.8	0.018	2.9	0.029	6.3	0.065
2	2.7	.014	6.4	.033	14.8	.080
3	..	...	5.7	.020	23.7	.090
3.25	5.0	.016	..	...	..	...
4	5.3	.014	..	...	27.5	.080
4.1	..	...	11.7	.030	..	...
5	7.2	.015	14.7	.031	38.1	.093
6	9.2	.016	..	...	..	...
6.4	..	...	22.4	.040	..	...
	Average	.016		.032		.080

Complete Pyrolysis of Triphenylmethyl Methyl and Triphenylmethyl Ethyl Ethers.—A sample of the methyl ether (25.24 g.) was heated at 280–300° in an apparatus designed to collect and measure the gaseous and liquid products of the decomposition. The rate of decomposition increased to a maximum between the 88th and 137th hours, decreased, and was complete in 240 hours. There was obtained 1.6 g. of a liquid boiling at 64–65° which was identified as methyl alcohol by the melting point of the *p*-nitrobenzoate prepared from it (95°). A mixed melting point confirmed the conclusion. The gas measured 934 cc. (24° and 761 mm.) and was shown by analysis to contain 87.2% of carbon monoxide; the remaining gas which was not combustible and which contained only a trace of carbon monoxide was evidently the nitrogen present in the apparatus. The residue, of a brown color, was shown to be triphenylmethane and a trace of a colored substance. From 0.0925 mole of ether were obtained 0.0329 mole of carbon monoxide and 0.0399 mole of methyl alcohol; 36% of the ether yielded these products and triphenylmethane and the rest formaldehyde and the hydrocarbon. Fifteen grams of the ethyl ether was pyrolyzed under the same conditions. The carbon monoxide formed measured 50 cc., which corresponds to a decomposition of about 4% to produce this gas.

Effect of the Products of Decomposition on the Rate of Pyrolysis.—Since the increase in the rate of pyrolysis with time was most marked in the case of the methyl ether, the influence of the presence of triphenylmethane on the rate was studied with this compound. A mixture of the ether and the hydrocarbon in the molecular ratio of 2:1 was melted and stirred to ensure homogeneity. After solidification weighed portions were heated and analyzed in the manner described above. The results were as follows: at 269° the ratios between the percentage decomposition in the presence and in the absence of the hydrocarbon were at the end of two hours 2.0, four hours 1.5 and five hours 1.3. At 280° the ratios after the same time intervals were 3.6, 2.5, and 2.3, respectively. The results show that the presence of the chief product of the pyrolysis markedly accelerates the rate of pyrolysis and are consistent with the fact that when the ether alone is used the rate of decomposition increases with time.

Similar experiments were made in which methyl alcohol and formaldehyde were added to the ether before pyrolysis. In the case of the former there appeared to be a slight retarding effect, but the results were such that a definite statement is not warranted. When formaldehyde was used the results were not conclusive.

Effect of Air and Oxygen on the Rate of Pyrolysis.—All the experiments recorded above were carried out in sealed tubes which contained in addition to the ethers approximately 5 cc. of air. Determinations of rates were made simultaneously with tubes that contained air and others that were evacuated and filled with nitrogen three times before sealing. In the case of the methyl ether at 268° the percentage decomposition in the presence of air at the end of three hours was 6.3 times that in the presence of nitrogen only; at the end of six hours it was 7.0 times as great. The amount of oxygen in the tubes containing air was so small that if it brought about oxidation to carbon dioxide the loss of weight resulting would be equivalent to 0.9%; if a volatile or non-volatile substance were formed the change in weight would be correspondingly small. At the end of six hours in the presence of air 12.7% of the ether had decomposed. The effect of oxygen is apparently catalytic and probably takes place through the intermediate formation of a peroxide.

To gain further information in regard to the influence of oxygen on pyrolysis the methyl ether was heated in tubes which were exhausted and filled with oxygen three times. The pyrolysis was carried out at 263°, which is one degree above the temperature at which the ether first shows signs of decomposition when it is heated in such a way that the temperature rises at the rate of one degree per minute. Control experiments were carried out at the same time with tubes filled with nitrogen. At the end of two, four and five hours the ratios of the percentage decomposition in the presence of oxygen and of air were 3.2, 4.4 and 2.8, respectively. The percentage decomposition in the presence of oxygen at the end of five hours was 32.5.

Summary

1. The rates of pyrolysis of the methyl, ethyl, and isopropyl ethers derived from triphenylcarbinol have been determined at several temperatures.

2. The ethyl ether at the lower temperatures and up to about 11% decomposition showed the characteristics of a reaction of the first order and the rate doubled for a rise of 10 degrees. Similar results were obtained with isopropyl ether up to about 28% decomposition.

3. The calculated first order velocity constants in the case of the methyl ether increased rapidly with time. It was shown that triphenylmethane, a product of the decomposition, had a marked accelerating effect on the decomposition.

4. The presence of a small amount of air increased greatly the rate of pyrolysis.

CAMBRIDGE, MASSACHUSETTS

RECEIVED AUGUST 2, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

Basis for the Physiological Activity of Onium Compounds. XV. Sulfonium Compounds[1,2]

BY R. R. RENSHAW AND D. S. SEARLE

In earlier work[3] it was found that one of the derivatives of the sulfur analog of choline (acetylthioformocholine) produced a very marked lowering of the blood pressure (muscarine action) and that this action was not complicated, as is the case with most of the choline derivatives, by the evidence of any stimulating nicotine action. The need of an effective product having this type of action is considerable in therapeutics. The authors, in coöperation with Reid Hunt, have, therefore, undertaken to investigate a number of sulfonium derivatives.

The successful preparation of sulfonium compounds by the direct addition of a halide to a sulfide is in general restricted to the relatively simple compounds. One difficulty, as has been pointed out in an earlier paper,[4] is the tendency of the unsymmetrical sulfonium structures to dissociate in two or more ways and of the products then to recombine to produce a mixture difficult or impossible to separate. Often, too, the dissociation is

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(1) This problem is being carried out in coöperation with Dr. Reid Hunt of the Harvard Medical School. The physiological data are the basis of another series of papers published elsewhere by him.

(2) This is the first paper from a thesis presented by D. S. Searle, June, 1930, for the degree of Doctor of Philosophy at New York University.

(3) Hunt and Renshaw, *J. Pharm. Exptl. Therap.*, **25**, 315 (1925).

(4) Renshaw, Bacon and Roblyer, THIS JOURNAL, **48**, 517 (1926).

rapid and the equilibrium point well over toward the dissociation products which tend to form uncrystallizable oils with the sulfonium compounds present. When heavy groups are involved condensation takes place very slowly and in some cases apparently not at all after considerable time. Salsbury[5] was unable to condense β-bromo-ethyl acetate with ethyl, propyl or butyl sulfides as was evident by the fact that neither a solid nor an oil was precipitated after adding an excess of toluene to the reaction of mixtures which had stood several weeks. We were unable, too, to obtain appreciable condensation of benzyl or phenyl sulfides with β-bromoethyl phenyl ether.

A partial solution of the difficulties was obtained by taking advantage of an observation of Smiles[6] that in the presence of mercuric iodide sulfonium formation takes place rapidly with the production of the sulfonium-mercuric iodide double salt. By using this procedure, it has been possible to prepare the mercuric iodide or bromide double salts of a number of sulfonium compounds the simple onium salt of which could not be formed directly. In a number of cases, however, it was impossible or very difficult to isolate the free sulfonium compound after precipitating the mercury on account of the easy dissociation of the latter. Since the alkyl derivatives of the oxygen acids do not show the ready addition to the onium elements that the halides do it was thought that the oxygen acid salts of the onium compounds would likely be very stable. This was found to be the case and the sulfonium compounds were easily isolated as the stable nitrates or sulfates by first converting the double mercury halide salts into salts of these acids as described in the experimental part.

Experimental Part

The sulfides were condensed with molecular equivalent amounts of halide and mercuric salt using acetone or alcohol as the solvent. The double salts thus formed are soluble in acetone, insoluble in water, alcohol and ether. Details of the procedure for each case will be found in notes to Table I.

TABLE I

SULFONIUM COMPOUNDS

	M. p., °C.	Analyses, N Calcd.	Analyses, N Found	
$(C_6H_5CH_2)_2S(NO_3)CH_3$[a]	79	4.81	4.83	4.89
$(C_6H_5CH_2)_2S(NO_3)CH_2COOC_2H_5$[b]	120	3.86	3.85	3.81
$(C_6H_5)_2S(NO_3)CH_3$[c]	108	5.32	5.22	5.33
$(CH_3)_2S(NO_3)CH_2CH_2OC_6H_5$[d]	62–65	5.71	5.60	6.10
		Analyses for Br		
$(C_2H_5)_2S(Br)CH_2CH_2OC_6H_5 \cdot HgBr_2$[e]	78	36.81	36.88	36.75
$(C_3H_7)_2S(Br)CH_2COOC_2H_5$[f]	70	28.02	28.00	27.95
$(C_6H_5CH_2)_2S(Br)CH_2COOC_2H_5 \cdot HgBr_2$	127	32.34	32.39	...

[a] Prepared from $(C_7H_7)_2S(I)CH_3 \cdot HgI_2$, m. p. 155°, which was obtained in nearly quantitative yield by condensing $(C_7H_7)_2S$ with CH_3I and HgI_2 in acetone as described

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(5) Salsbury, Master's Thesis, New York University, 1927.

(6) Smiles, *J. Chem. Soc.*, 77, 160 (1900).

by Smiles and Rossignol. The nitrate first formed as an oil which solidified on stirring with absolute ether.

[b] From $(C_7H_7)_2S(Br)CH_2COOC_2H_5{\cdot}HgI_2$, m. p. 120°, or from $(C_7H_7)_2S(Br)CH_2COOC_2H_5{\cdot}HgBr_2$. The dibenzyl sulfide, ethyl bromoacetate, and mercuric halide were condensed in acetone solution by heating the solution in a steam-bath for about half an hour, then after standing several days precipitating the double salt by the addition of alcohol. The free nitrate formed as a white crystalline solid on the addition of ether to the final filtrate, no oil forming at any time.

[c] From $(C_6H_5)_2S(I)CH_3{\cdot}HgI_2$, m. p. 95°, which was obtained by condensing $(C_6H_5)_2S$, CH_3I and HgI_2, in acetone solution as described under *b* above.

[d] From $(CH_3)_2S(Br)CH_2CH_2OC_6H_5{\cdot}HgBr_2$, obtained by condensing $(CH_3)_2S$, $BrCH_2CH_2OC_6H_5$ and $HgBr_2$ in alcohol solution. It was found that acetone was not suitable for this condensation since insoluble $(CH_3)_2S{\cdot}HgBr_2$ formed instead of the sulfonium salt. This sulfide complex was soluble in alcohol, however, and the best results were obtained when the alcohol was added to the reactants in quantity sufficient to dissolve them. The solution was then heated in a pressure bottle immersed in a steam-bath for several hours. A viscous oil formed and was separated and solidified by stirring with alcohol or ether. The substance was insoluble in alcohol, ether and water, but soluble in acetone, m. p. 70–71°. It did not decompose when heated to its melting point as the sulfide complex did. The yield was 81%. This double salt yielded the free nitrate first as an oil, which solidified on standing with absolute ether for a few hours. The nitrate was somewhat more hygroscopic than the other nitrates, which is due in part, perhaps, to its low m. p.

[e] This double salt was prepared in a manner analogous to that described above in *d*. The free nitrate could be obtained only as a gummy semi-solid. As noted above the corresponding dimethyl compound was somewhat hygroscopic and of low melting point (70°). It would be expected therefore that the diethyl compound would have an even lower melting point and be more hygroscopic.

[f] Prepared by Salsbury by direct condensation.

The double salts were in each case dissolved in acetone and an excess of solid silver nitrate was added and stirred until no more silver bromide or iodide formed. The filtered solution was then treated with hydrogen sulfide until precipitation of mercuric sulfide and silver sulfide was complete. The solution was filtered and ether was added to precipitate the sulfonium nitrate. The nitrates were white crystalline solids soluble in water, alcohol and acetone, and insoluble in ether. These nitrates appear to be very stable, and on long standing are free of odor or other evidence of dissociation so characteristic of sulfonium halides. Once obtained in dry form they exhibit little or no tendency, for the most part, to be very hygroscopic.

Summary

1. A method has been described for the preparation of crystalline, stable sulfonium compounds.

2. Several new sulfonium compounds have been prepared as mercuric halide double salts and as nitrates. The halogen salts of many of the sulfonium compounds undergo onium dissociation so readily that they cannot be isolated in a crystalline form. The nitrates are much more stable, showing little or no tendency to undergo this dissociation under ordinary conditions. They are also much less hygroscopic.

NEW YORK, N. Y.

RECEIVED AUGUST 4, 1933
PUBLISHED DECEMBER 14, 1933

[Contribution from the Insecticide Division, Bureau of Chemistry and Soils]

Replacement of the Diazo Group by the Acetoxy Group

By H. L. Haller and P. S. Schaffer

In the course of preparing some organic fluorine compounds by the excellent method of Balz and Schiemann,[1] which consists in the thermal decomposition of aryldiazonium borofluorides, it was found that *m*-chlorophenyldiazonium borofluoride interacts with acetic acid or acetic anhydride, with the elimination of nitrogen, to give *m*-chlorophenyl acetate in a yield of about 50%. *m*-Bromophenyldiazonium borofluoride behaved similarly and *p*-acetaminophenyldiazonium borofluoride with acetic anhydride gave diacetyl-*p*-aminophenol in a yield of about 52%.

The replacement of the amino group by the acetoxy group through the diazo reaction has been accomplished by the decomposition of dry diazo salts with glacial acetic acid,[2] or with acetic anhydride,[3] and by the diazotization of an amine in warm glacial acetic acid.[4] In either case the yield is poor. Moreover, when the dry diazo salts are employed, they are, as a rule, difficult to prepare and unstable. On the other hand, the aryl diazonium borofluorides have been shown[1] to be stable, easy to handle, and readily prepared.

The exact mechanism of the reaction is not known, but it probably takes place in the following manner

$$C_6H_5N_2BF_4 + CH_3COOH \longrightarrow C_6H_5OOCCH_3 + N_2 + BF_3 + HF$$

With *p*-acetaminophenyldiazonium borofluoride and acetic anhydride, the compound which is first obtained contains boron and fluorine. The product is probably a coördination compound of diacetyl *p*-aminophenol and boron trifluoride. On recrystallization from water or dilute alcohol the product loses boron and fluorine, and diacetyl-*p*-aminophenol is obtained.

As the aryl acetates are readily hydrolyzed to the corresponding phenols, the reaction provides a ready method of replacing the amino group by the hydroxy group when the normal decomposition of the diazo compound with water does not take place easily.

Experimental

_m_-Chlorophenyldiazonium Borofluoride.—This compound was obtained from a solution of *m*-chlorophenyldiazonium chloride and a 40% solution of hydrofluoroboric acid in a yield of 93%. It decomposed at 157° (uncorr.).

_m_-Chlorophenyl Acetate.—Twenty grams of *m*-chlorophenyldiazonium borofluoride was heated gently under reflux in 100 cc. of glacial acetic acid until nitrogen began to be evolved. After the vigorous reaction had subsided, the solution was boiled

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(1) Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

(2) Orndorff, *Am. Chem. J.*, **10**, 368 (1888).

(3) Wallach, *Ann.*, **235**, 233 (1886).

(4) Meldola and East, *J. Chem. Soc.*, **53**, 460 (1888).

for five minutes, cooled and concentrated under reduced pressure to remove most of the acetic acid. Water was then added, and the solution was neutralized with solid sodium carbonate and extracted with ether. The ether extract was washed with water and dried over sodium sulfate. After the removal of the ether the remaining oil was distilled. It boiled at 84–86°, p = 2 mm.; at 108°, p = 12 mm. The yield was 7.5 g.

Anal. Calcd. for $C_8H_7O_2Cl$: Cl, 20.8. Found: Cl, 21.1.

p-Acetaminophenyldiazonium Borofluoride.—This compound was obtained from a diazotized solution of p-acetaminoaniline and a 40% solution of hydrofluoroboric acid in a yield of 84%. It decomposed at 135° (corr.). It can be recrystallized from acetone–chloroform solution.

Diacetyl-p-aminophenol.—Twelve and a half grams of p-acetaminophenyldiazonium borofluoride in 65 cc. of acetic anhydride was heated under reflux until nitrogen was no longer given off. The reddish-brown solution deposited a crystalline product on cooling. This was filtered off and washed with acetic anhydride. It contained boron and fluorine, but it gradually lost them on heating. On recrystallization from water a product free from boron and fluorine was obtained. It melted at 151.5–152.5° (corr.). When mixed with an equal quantity of authentic diacetyl-p-aminophenol, there was no depression of the melting point.

Anal. Calcd. for $C_{10}H_{11}O_3N$: N, 7.25. Found: N, 7.23.

The acetic anhydride filtrate was concentrated under reduced pressure to remove most of the acetic anhydride. The concentrated solution was then worked up as described for the m-chlorophenylacetate. Two grams of diacetyl-p-aminophenol was obtained. The total yield of diacetyl-p-aminophenol was 5 g., 52%.

The p-acetaminophenyl diazonium borofluoride can also be converted to diacetyl-p-aminophenol by the use of acetic acid. In some experiments the crude diacetyl-p-aminophenol melted at 113–116° (uncorr.). A pure product was obtained only on sublimation.

Summary

m-Chlorophenyldiazonium borofluoride reacts with acetic acid to give m-chlorophenyl acetate.

p-Acetaminophenyldiazonium borofluoride interacts with acetic anhydride to give diacetyl-p-aminophenol.

Since the aryl acetates are readily hydrolyzed to the corresponding phenols, the reaction provides a ready method of replacing the amino group by the hydroxyl group when the normal decomposition of the diazo body with water does not take place.

WASHINGTON, D. C.

RECEIVED AUGUST 7, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NORTH CAROLINA]

The Identification of Mercaptans with 2,4-Dinitrochlorobenzene. II

BY R. W. BOST, J. O. TURNER AND M. W. CONN

In a previous paper[1] it was shown that 2,4-dinitrochlorobenzene is a valuable reagent for the identification of mercaptans. In view of the favorable reception which this reagent has received, the authors submit herewith an additional list of mercaptan derivatives.

The method of preparation of both the sulfides and the sulfones was the same as given in the previous paper.[1] The sulfides of the mono-thiols are odorless, and consist of golden yellow needles while those of the dimercaptans are amorphous. All have definite melting points. The derivatives of the mono-thiols were purified from alcohol. It was necessary to recrystallize lauryl dinitrophenyl sulfide several times from alcohol to obtain a constant melting point. The derivatives of the dimercaptans were recrystallized from nitrobenzene. The sulfones are snow white, felty needles with sharp melting points. They were purified by recrystallization from alcohol.

TABLE I

DERIVATIVES OF MERCAPTANS WITH 2,4-DINITROCHLOROBENZENE

Mercaptan	M. p., °C. (corr.)	Sulfur analyses, % Calcd.	Sulfur analyses, % Found	Mercaptan	M. p., °C. (corr.)	Sulfur analyses, % Calcd.	Sulfur analyses, % Found
Decyl	85	9.41	9.55	β-Thionaphthol	145	9.81	9.42
Undecyl	90	9.04	8.92	Cyclohexyl	148	11.34	11.05
Lauryl	89	8.69	8.52	Ethylene thiohydrin	100.5	13.11	13.25
Allyl	71.5	13.33	13.60	Dimethylene di-	248	15.04	14.86
o-Thiocresol	101	11.05	11.08	α-Methyl dimethylene di-	226	14.57	14.35
m-Thiocresol	90.5	11.05	10.87	Trimethylene di-	194	14.57	14.36
p-Chlorothiophenol	123	10.30	10.05	Tetramethylene di-	176	14.09	14.17
p-Bromothiophenol	142	9.01	9.29	Pentamethylene di-	170	13.69	13.80
α-Thionaphthol	176	9.81	9.45	Hexamethylene di-	218	13.29	13.26

TABLE II

SULFONES OF 2,4-DINITROPHENYL THIOETHERS

Sulfone	M. p., °C. (corr.)	Sulfur analyses, % Calcd.	Sulfur analyses, % Found
Decyl	93	8.60	8.46
Undecyl	97	8.29	8.18
Lauryl	101	7.99	7.96
Cetyl	105	7.07	6.91
o-Thiocresol	155	9.93	9.81
m-Thiocresol	144.5	9.93	10.00
p-Chlorothiophenol	170	9.34	9.43
p-Bromothiophenol	190	8.27	8.40
Cyclohexyl	172	10.19	10.05

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(1) Bost, Turner and Norton, THIS JOURNAL, 54, 1985 (1932).

The authors are indebted to Dr. C. R. Noller, of Stanford University, who kindly furnished us with samples of decyl, undecyl and lauryl mercaptans for this work.

Summary

1. 2,4-Dinitrochlorobenzene, a reagent previously proposed by the authors, has now been studied more extensively and found to be valuable for both mono- and di-mercaptans.

2. Melting point and analyses are presented for eighteen 2,4-dinitrophenyl alkyl and aryl thio-ethers. In addition, data are presented for nine of the corresponding sulfones.

CHAPEL HILL, N. C.

RECEIVED AUGUST 7, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Mechanism of Carbohydrate Oxidation. XVI.[1] The Action of Aqueous Solutions of Potassium Hydroxide on *l*-Rhamnose

BY GALE FRANCIS NADEAU, MILDRED RATLIFF NEWLIN AND WM. LLOYD EVANS

Since *l*-rhamnose differs from *l*-mannose by having a methyl group in place of the primary alcohol group of the hexose sugar, it follows that the behavior of rhamnose toward aqueous solutions of potassium hydroxide must have certain restrictions placed upon it when this sugar is considered as a possible source of lactic acid through its reaction with the base. Among these limitations is the structural inability of the rhamnose molecule to form two molecules of glyceric aldehyde which in turn are partially converted into pyruvic aldehyde, the precursor of lactic acid. To determine the general extent to which the presence of the methyl group prevents *l*-rhamnose from acting like the hexose sugars in this respect was the first objective in this work.

It has been shown previously in this series of studies that the temperature employed and the concentration of the alkali used exercise marked effects in the yields of lactic acid obtained from certain sugars when they are subjected to the action of potassium hydroxide solutions, during forty-eight hours, a period of time which seemed sufficient to indicate the general tendency of the various sugars studied under these conditions.[2] To ascertain if this was equally true for *l*-rhamnose was the second objective in this work.

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[1] Contribution XV of this Series, THIS JOURNAL, **54**, 698 (1932).

[2] Evans and co-workers, (a) THIS JOURNAL, **48**, 2665 (1926); (b) **48**, 2703 (1926); (c) **50**, 486 (1928); (d) **50**, 1496 (1928); (e) **50**, 2543 (1928); (f) **52**, 294 (1930); (g) **52**, 3680 (1930); (h) **53**, 4384 (1931).

Experimental Part

(a) **Reagents.**—All the reagents used in these experiments were examined for their purity by the usual well-known laboratory procedures.

(b) **Rhamnose.**—Most of the rhamnose was prepared from lemon flavine by Walton's[3] method. The purity of the product (m. p. 92°, $[\alpha]^{20}_{D}$ 8.9°) was determined by the procedures of Pfanstiehl and Black.[4] Chlorides, alkaline earths and heavy metals were absent.

(c) **Apparatus and Analytical Procedures.**—The general and analytical procedures used throughout this work were essentially the same as those described in previous reports,[2b] except for the modification adopted in the method for the determination of lactic acid.

An amount of *l*-rhamnose equal to 2.2763 g. was weighed into a 150-cc. carbon dioxide flask. Twenty-five cc. of standard potassium hydroxide was added, the flask stoppered immediately, and placed in a thermostat at the desired temperature for forty-eight hours. The flasks were then removed, packed in ice, and 25 cc. of standard phosphoric acid added dropwise to the reaction mixture. Standard phosphoric acid solutions were prepared of the same molar strength as each of the potassium hydroxide solutions. The titer value of the acid solution against the corresponding alkali solution was determined by titrating 25 cc. of the alkali solution with the phosphoric acid, using methyl orange as indicator. The end-point appears when the primary potassium salt is formed. The color was compared with the color of an aqueous solution of primary potassium phosphate and methyl orange. There was considerable difficulty in observing the end-point when the solutions were stronger than two normal, due to the buffer action of the phosphates formed. In these cases the acid and alkali solutions were diluted, and the diluted solutions were titrated against each other. This procedure introduced no error and made the titration more accurate. The solution was transferred to a 500-cc. round-bottomed flask and the volatile products distilled off under reduced pressure at a temperature not exceeding 50°.

For the determination of lactic acid 60 cc. of water was added to the dry residue and the solution digested with norite for half an hour on a boiling water-bath. The material was then filtered, the residue washed with hot water and the filtrate evaporated sufficiently to be placed in a Soxhlet extractor. In a Sy flask was placed 75 cc. of water and an excess of zinc carbonate. The acid solution was extracted for forty-eight hours with U. S. P. ether. The Norite treatment removes a great deal of the tarry material which is otherwise extracted along with the ether-soluble acids and carried into the lower flask. The removal of the tar is not complete and the water solutions in the Sy flasks vary in color from a very pale straw color in the lower temperature runs to a dark amber in the runs at seventy-five degrees.

At the completion of the extraction the ether remaining in the Sy flask was evaporated. Norite was added to the material in the flask and the mixture boiled for several minutes to complete the reaction between the lactic acid and zinc carbonate. The solution was filtered from excess zinc carbonate and Norite, the residue washed with hot water and the filtrate evaporated to small volume on a water-bath. The second treatment with Norite serves further to decolorize the solutions, and although the runs with more dilute alkali at both 50 and 75° still retain some tar, it is not sufficient to interfere with the crystallization of the zinc lactate, and it is possible to wash the salt practically free from impurities.

When the zinc lactate had crystallized from the concentrated solutions, the material was cooled in ice and salt, then filtered into a weighed, porous-bottomed Gooch

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(3) Walton, THIS JOURNAL, 43, 127 (1921).

(4) Pfanstiehl and Black, *Ind. Eng. Chem.*, 13, 685 (1921).

crucible, washed with a little ice-water, then cold 95% alcohol, and finally ether, and air-dried. We found that zinc lactate tends to dehydrate by overnight drying *in vacuo* at 60–65°. The purity of the zinc lactate was determined in the usual way by roasting a sample to zinc oxide. The percentage carbon return as lactic acid with six different normalities of potassium hydroxide at 25, 50 and 75° are shown in Fig. 1.

As it appeared possible that either lactic acid or zinc lactate might be adsorbed by the Norite with a consequent lowering of the results, a run was made with glucose and 3 N alkali at 50°. Under these conditions Evans and O'Donnell[2e] report a carbon return as lactic acid equal to 45.1%. Using Norite as described above the yield of zinc lactate indicated a carbon return of 45.6%.

Before Norite was used the solutions of zinc lactate after extraction were always colored dark brown by the tar present. An attempt was made to get rid of this tar by placing these solutions in turn in the extractor and extracting again with ether. This removed part of the color, but apparently the tars are less soluble in ether after the reaction with zinc carbonate. The extract so obtained was dissolved in water. This solution gave no precipitate of zinc sulfide when treated with hydrogen sulfide in the presence of ammonia, indicating that none of the zinc salts had been extracted. This aqueous solution was acid to litmus and reduced Fehling's solution.

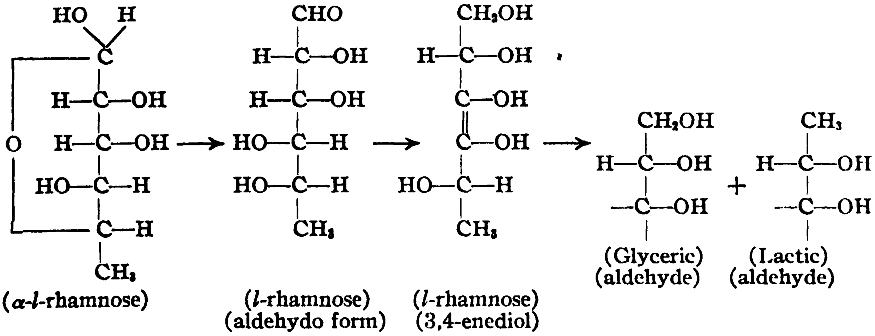
Some of the Norite was roasted to an ash which was taken up in dilute hydrochloric acid and tested for the presence of metallic ions. Analysis showed that the ash contained small amounts of iron, aluminum and zinc.

The phosphate solutions remaining after the ether extraction were tested, by the use of Fehling's solution, for the presence of reducing substances. In every case there was evidence of reduction, varying from copious precipitates of cuprous oxide from the twenty-five degree runs to a bare trace with the 7 N potassium hydroxide at 75°. No experiments were made to determine to what extent this reduction was due to unchanged sugar. Rhamnose is undoubtedly present especially at the lower alkalinities, because it has been previously shown that some of the sugar conversions caused by alkali go on for a long period of time.

Discussion and Summary

If aqueous solutions of potassium hydroxide react toward rhamnose in the same general manner as previously observed in the case of certain disaccharides,[2f,h] hexoses,[2d,e] pentoses[2g] and trioses[2b,c] then the data obtained from the interaction of the alkaline solutions of the methylpentose should be in accord with the enediol theory of carbohydrate chemical behavior. In these experiments various reaction mixtures were examined for their content of lactic acid while others were studied for their production of pyruvic aldehyde. The data with reference to these products are discussed in the following paragraphs.

l-Rhamose-3,4-enediol: (a) Lactic Acid.—If rhamnose forms a 3,4-enediol in alkaline solutions of appropriate normality, then it is theoretically conceivable that this compound could undergo fission at the double bond and thus give rise to the formation of two different aldehydes, namely, glyceric and lactic. From this standpoint, the chief chemical interest lies in this latter possibility, because in the hexose sugar molecules such a change as that described would give rise to two molecules of one and the same aldehyde, namely, glyceric, while in rhamnose the products of such a reaction would be one molecule of glyceric aldehyde and one of lactic aldehyde. These changes in the *l*-rhamnose molecule are shown in the following reactions. It has been pointed out repeatedly that glyceric aldehyde is[2] an intermediate compound in the production of lactic acid formed through the interaction of certain sugars and alkalies. Hence, it follows that at least one-half of the *l*-rhamnose carbon should be found in these reaction mixtures as lactic acid if it were not for other changes taking place between the rhamnose molecule and its decomposition products and the aqueous solutions of the potassium hydroxide.



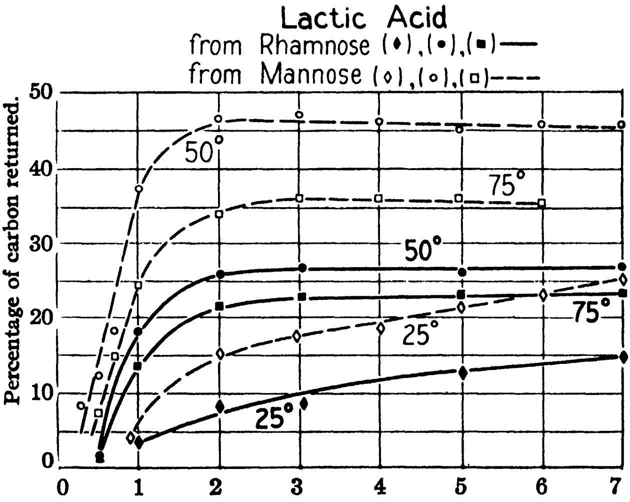


Fig. 1.

That lactic acid may actually be obtained in alkaline solutions of *l*-rhamnose is shown in Fig. 1, in which the data with reference to the experimental yields obtained at 25, 50 and 75° are conveniently recorded as functions of the *original* alkali normality, a value which will necessarily decrease due to the formation of acid in the reaction mixture. The general tendency of the yields of this acid at 75° to be lower than those at 50° is also characteristic of certain hexoses,[2e] pentoses[2g] and the trioses[2b,c] when these carbohydrates are subjected to the same experimental conditions as were employed with rhamnose. An examination of the lactic acid data shows that the production of this acid from *l*-rhamnose seems to be dependent upon the same general experimental factors, namely, temperature and alkali concentrations, as were observed in the case of other sugars previously studied. Shaffer and Friedemann[5] have shown that the concentration of the sugar itself is also an important factor governing the yields of lactic acid.

It is clear that in the presence of an appropriate oxidizing agent the two fragments resulting from the fission of the rhamnose 3,4-enediol should yield glyceric and lactic acids. In the absence of an oxidizing agent, however, lactic aldehyde would probably be incapable of existence by reason of its rearrangement into acetol. It is planned to study any possible effects of the small amount of atmospheric oxygen contained in the reaction flask in the formation of reaction products, such as formic and acetic acids. Nef[6] showed that acetol under the influence of alkalies would form resins *without the production of lactic acid.* This observation has been verified recently by Dworzak and Prodinger,[7] who found that crystalline lactic aldehyde in 4% sodium hydroxide solution gave a brown sirup. The distillate in our work gave only the faintest odor of iodoform with the usual alkaline iodine reaction.

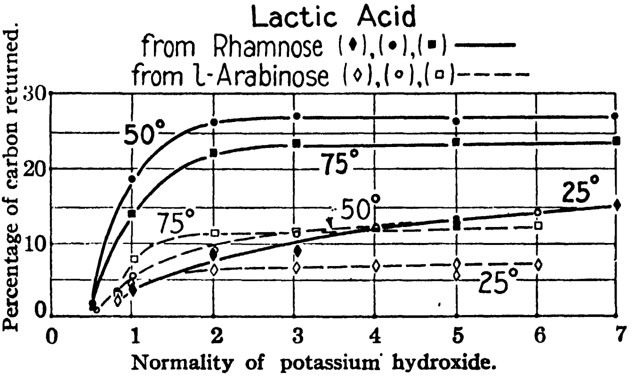


Fig. 2.

Since the arabinose molecule has the possibility of yielding but one molecule each of glyceric aldehyde and glycol aldehyde, rhamnose one each of glyceric and lactic aldehydes, and that of mannose two molecules of glyceric aldehyde, one would expect that the yields of lactic acid from rhamnose would resemble more nearly those of arabinose than those of

(5) Shaffer and Friedemann, *J. Biol. Chem.*, **86**, 345 (1930).

(6) Nef, *Ann.*, **335**, 254 (1904).

(7) Dworzak and Prodinger, *Monatsh.*, **50**, 459–475 (1928).

mannose if all the conditions within the reacting mixtures were ideal, *i. e.*, if these various sugars reacted with the same degree of ease toward the alkali present. In Fig. 2 a comparison of the yields of this acid obtained from *l*-arabinose and *l*-rhamnose at 50° shows that relatively the rhamnose seems to react more like a hexose sugar than a pentose one. It is known that the yields of lactic acid arising from the alkaline degradation of glucose and mannose[2e] at 50° are of about the same order of magnitude, while the yields obtained from glucose, mannose and fructose[2d,e] at 75° are also approximately the same. Therefore, these data and those plotted in Figs. 1 and 2 show that the yields of lactic acid from rhamnose lie between those of the above named hexoses and arabinose[2g] at 50 and 75°. In the case of xylose[2g] the yields of lactic acid are still higher than those from arabinose. Since *l*-rhamnose, *l*-isorhamnose and the unknown *l*-2-keto-rhamnose (or in the more convenient nomenclature of Votoček[8] *l*-manno-methylose, *l*-gluco-methylose and *l*-fructo-methylose) are related to each other in the same way as glucose, mannose and fructose, and since the relation of the lactic acid curves at 50 and 75° are related to each other like those of these well-known hexose sugars, it is very probable that the 75° lactic acid curve of *l*-rhamnose is approximately that for the other two related methyl pentoses.

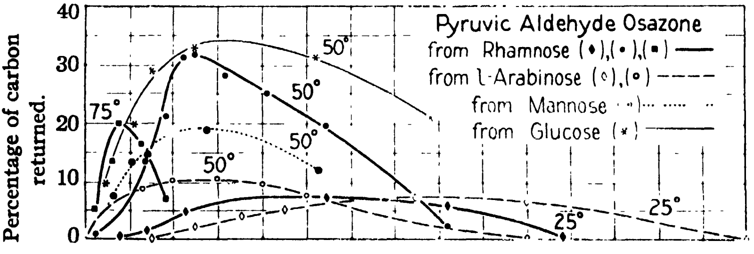


Fig. 3.

(b) Pyruvic Aldehyde.—If the behavior of rhamnose in alkaline solutions of appropriate normality is correctly expressed by the above equation, then it follows that there are two different possible sources for the formation of pyruvic aldehyde. (1) It is well known that glyceric aldehyde will form this compound under the experimental conditions employed. (2) Since lactic aldehyde will yield the same phenyl-osazone as pyruvic aldehyde and acetol then it is to be expected that rhamnose should more nearly resemble the hexose sugars in this respect than it does the pentose ones.

In Fig. 3 it is shown that rhamnose seems to have undergone the necessary transformations to yield pyruvic aldehyde osazone and that the yields are influenced by the temperature and the concentration of the alkali

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(8) Votoček, *Bull. soc. chim.*, [4] 43, 1 (1928).

employed. At 75° the maximum is much lower than at 50°. This is in harmony with the relative yields of lactic acid obtained from this sugar. Furthermore, it is evident that rhamnose and glucose[2e] at 50° will yield pyruvic aldehyde osazone in amounts that are of the same general magnitude. There is no way to differentiate between glyceric and lactic aldehydes as the sources of pyruvic aldehyde osazone in the case of rhamnose. It is clear from Fig. 3 that rhamnose is more like the hexoses than it is arabinose in this respect. Evans and Conaway have shown that arabinose and xylose are likewise much the same. The interest that attaches to the comparison with mannose lies in the fact pointed out above, namely, the substitution of the primary alcohol group in mannose for the methyl group of rhamnose—the asymmetrical portion of each molecule being the same.

Concerning the mechanism suggested by Evans and Hass[2e] for the conversion of glyceric aldehyde to pyruvic aldehyde, it has been pointed out by Mr. Harry Gehman of this Laboratory that the same end could be attained through the hydrogen of the water molecule reducing the primary alcohol group and the oxygen forming an aldehyde group on the other terminal carbon atom of the postulated intermediate oxidic ring.[9]

Acknowledgment.—In conclusion the authors wish to acknowledge their great indebtedness to The Cyrus M. Warren Fund of The American Academy of Arts and Sciences for very valuable assistance rendered during the progress of these experiments.

(9) *Cf.* Bernhauer, "Grundzüge der Chemie und Biochemie der Zuckerarten," Verlag von Julius Springer, Berlin, 1933, p. 118.

COLUMBUS, OHIO

RECEIVED AUGUST 10, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Phthaloylnaphthol with Hydroxylamine and with Diazomethane[1]

BY LOUIS F. FIESER

The exact nature of the two carbonyl groups of phthaloylnaphthol is still an open problem. The Grignard reagent appears to attack only one of the two ketonic groups,[2] and a further peculiarity is to be found in the anomalous, and still unexplained, course of the oxidation.[3] It thus seemed of interest to study the action of some other carbonyl reagent, and hydroxylamine was selected for the purpose. It was found that phthaloylnaphthol may be converted in an alkaline medium into either one or the other of two monoximes, and that a dioxime is not formed under any of the conditions investigated. The most striking observation to be recorded in this

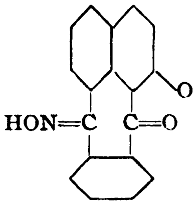
(1) Seventh paper. Sixth paper: THIS JOURNAL, 55, 3342 (1933).

(2) Fieser, *ibid.*, 53, 3546 (1931).

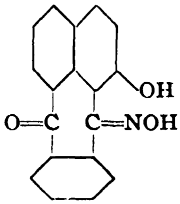
(3) L. F. and M. Fieser, *ibid.*, 55, 3010 (1933).

connection is that phthaloylnaphthol and hydroxylamine combine in cold alkaline solution to form an addition product composed of equivalent quantities of the two reactants. The formation of this remarkable substance will be described and discussed later, and it is mentioned at this point only in order to indicate the importance of considering in some detail the nature of the two oximes.

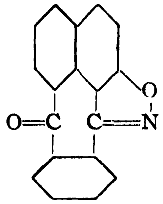
In a hot alcoholic solution, and in the presence of only a small amount of alkali, phthaloylnaphthol is converted exclusively into an oxime to which, for reasons to be indicated presently, we assign the structure of I. Adopting the new nomenclature,[3] according to which the starting material is named 1-hydroxy-7,12-pleiadenedione, this substance may be referred to as the "7-oxime." In the presence of considerably more alkali, some of this oxime is still produced, but the chief product is an isomeric substance which we regard as the 12-oxime, II, the reason being that it is easily converted into an anhydro compound, III. The dehydration is brought about by the action of strong mineral acids, by hot acetic anhydride, and by aqueous, but not alcoholic, alkali. It may be noted that this ready cyclization is in marked contrast to the behavior of the oxime of *o*-hydroxybenzophenone described by Meisenheimer and Meis.[4] The difference in behavior may be due to a difference in the spatial characteristics of the two molecules.



I



II



III

There is no evidence to show that the second oxime is not derived from a tautomeric, quinonoid form of phthaloylnaphthol, for an oxime group at position 1 could still combine with a hydroxyl group at position 12 with the production of an anhydro compound. It is known, however, that a quinonoid carbonyl group is less easily attacked by hydroxylamine than is the corresponding group of a diaryl ketone. This is shown by the behavior of the aroylanthraquinones on oximation. Thus the alternate structure appears to be a remote possibility and formula II, though not definitely proved, is given preference.

The first oxime might be a stereoisomer of the second one, but the evidence does not point in this direction. If this were true the isomers would probably be interconvertible, but this does not appear to be the case. A high alkalinity in an aqueous solution favors both the formation of II and its conversion into the sparingly soluble anhydro compound, but boiling alkali is without effect on the isomeric oxime. The compound is almost

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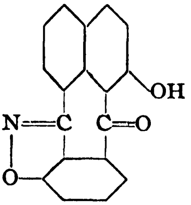
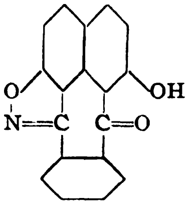
(4) Meisenheimer and Meis, *Ber.*, **57**, 289 (1924).

equally resistant to the action of strong sulfuric acid; it is unchanged at 100° and at 200° it is converted into an isomeric substance (not the 12-oxime) by a reaction which is probably of the Beckmann type. Under these conditions the 12-oxime would yield the stable anhydro compound.

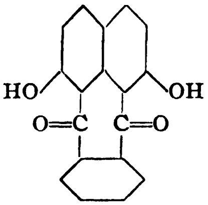
These facts point to the formula of a structural, rather than a spatial, isomer as indicated in I. One further observation may be cited which is at least consistent with this formulation. On being heated to 300°, the oxime in question is converted in part, possibly through a disproportionation, into a dehydro compound having the composition and the properties consistent with either formula IV or V. The compound corresponding to V was synthesized for comparison by the action of hydroxylamine in aqueous alkaline solution on the known[5] dihydroxy compound VI, and the two substances were found to be different. They are both of similar physical properties and both dissolve in alcoholic, but not in aqueous, alkali. Thus the product obtained from the 7-oxime may be assigned the structure of IV with a reasonable degree of confidence.



IV



V



VI

While the addition of hydroxylamine to the deep orange-yellow solution of phthaloylnaphthol in alkali or alcoholic alkali produces in the hot solution no noticeable change but results in the gradual production of an oxime, a striking and immediate color change occurs when the solution is at or below a temperature of 20–25° at the time when the reagent is added. The deep color at once disappears and the solution becomes very faintly yellow and acquires a purple fluorescence. Using an aqueous solution, and adding an excess of the amine in the form of the hydrochloride until the alkali present is neutralized, a micro-crystalline solid separates in quantitative yield. This is colorless when moist, but becomes pale yellow on drying. The composition is that of the sum of the two components, and the compound is easily re-converted into these substances. This breakdown occurs almost immediately on bringing the addition product into contact with acetic or hydrochloric acid. The substance dissolves very readily in cold alkali or in cold alcohol and the solutions are at first nearly colorless. On warming, the yellow phthaloylnaphthol is at once formed.

So unstable is the addition product that it can be dehydrated only under carefully controlled conditions. Treated with pyridine and acetic anhydride at a low temperature, it was converted in small part into the acetate of

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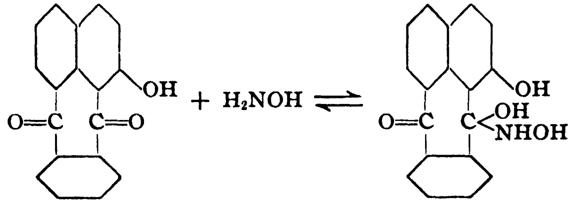
(5) Rieche, Sauthoff and Müller, *Ber.*, **65**, 1371 (1932).

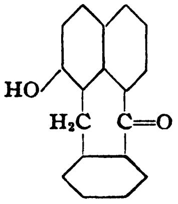
phthaloylnaphthol, but the chief product was an oxime diacetate, m. p. 163°. This on hydrolysis yielded the 12-oxime (II) in a pure condition. The diacetate of the isomeric oxime was not present in the acetylation mixture. That the reaction follows the simple course of dehydration followed by acetylation, without a preliminary breakdown and recombination of the components, is clearly shown by an experiment in which the addition product was heated with pyridine, and as a result of which both oximes were formed. Here there evidently is a preliminary breakdown of the molecule.

The addition product being thus related to the 12-oxime, it might at first be regarded as a simple hydrate of this oxime, formed by the addition of a molecule of hydroxylamine to the 12-carbonyl group of phthaloylnaphthol as indicated in the equation.

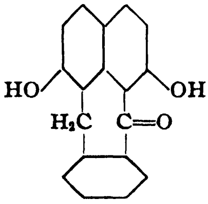


To this formulation, however, there are certain objections. In the first place it is improbable. The only compounds which are known to form such addition products (or hydrates) are substances of the type represented by chloral, which possesses an unusually reactive carbonyl group. It is difficult to imagine that the carbonyl group of the diaryl ketone in question possesses any such inherent additive capacity.

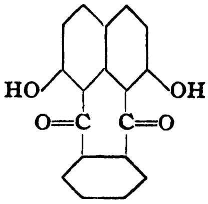
Further grounds for questioning the interpretation under discussion were furnished by a study of the two mono ketones VII and VIII. These are



VII



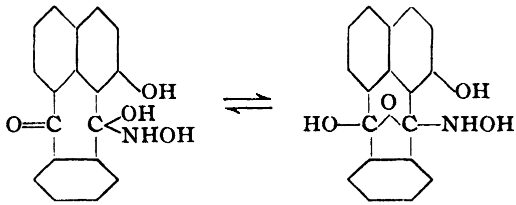
VIII



IX

both soluble in cold alkali and the solutions are highly colored, so that it would be easy to observe the formation of an addition product with hydroxylamine if such a reaction were to take place. In each case the test was negative. The carbonyl group of VII occupies a position in the molecule similar to that of the apparently reactive group of phthaloylnaphthol, and hence the failure of the compound to react might be attributed to the absence of an adjacent hydroxyl group, which might in some way induce reaction, possibly through a tautomerization. Such a group is present, however, in the dihydroxy compound VIII, and still no addition product is formed. These two mono ketones, indeed, do not even form oximes in a strongly alkaline, hot solution. A single carbonyl group flanked in this way by a naphthalene and a benzene nucleus, is if anything unusually unreactive.

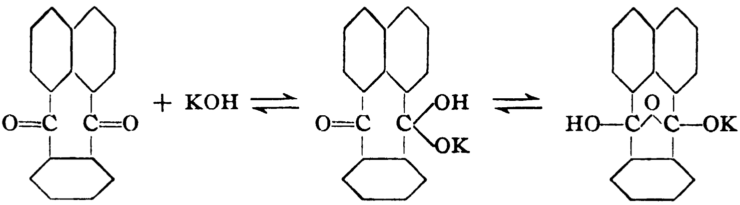
Why, then, does one carbonyl group of phthaloylnaphthol possess, or appear to possess, a reactivity of just the opposite degree? The answer in our opinion is to be found in a comparison of VIII with phthaloylnaphthol or, better, with the diketone IX which forms a similar hydroxylamine addition product. The only essential difference is that the latter compounds possess a second carbonyl group, and it may be inferred that this is a factor essential for the reaction. The influence can hardly be an indirect one, for the second carbonyl group is too far removed in the carbon chain from the first one. The second carbonyl group may, however, promote the reaction in a direct manner by accepting from the first group a part of the addenda. The reaction may be pictured as follows



The hypothesis of the formation of the oxygen bridge becomes particularly appealing on an examination of the space models. The carbon atoms concerned are so situated that the bridge can form without strain. According to this interpretation, the primary addition product probably forms as pictured in the first equilibrium shown above, but only to a very slight extent; the equilibrium is then displaced by the intramolecular addition of the hydroxyl group to the second carbonyl group.

It is of course equally possible that it is the amino hydrogen atom which enters into the second addition, with the production of a nitrogen rather than an oxygen bridge, but it is a difficult matter to make such a fine distinction. Various alkyl, aryl and acyl derivatives of hydroxylamine and also of hydrazine were tested in the hope of deciding the point, but the only other compound found to form an addition product was hydrazine. On the other hand, the following derivatives of 7,12-pleiadenedione were tested and in each case found to form hydroxylamine addition products: 1,2-dihydroxy-, 1,6-dihydroxy-,[5] 2,6-dimethyl-1-hydroxy- and 1-hydroxy-4,5-benz-7,12-pleiadenedione. The preparation of the new compounds mentioned here, and also of VIII, above, will be described in the eighth paper of the series. It may be said that all of the known alkali-soluble pleiadenediones exhibit the reaction. It is perhaps only a fortuitous circumstance that in all of these compounds there is a hydroxyl group adjacent to one of the carbonyl groups.

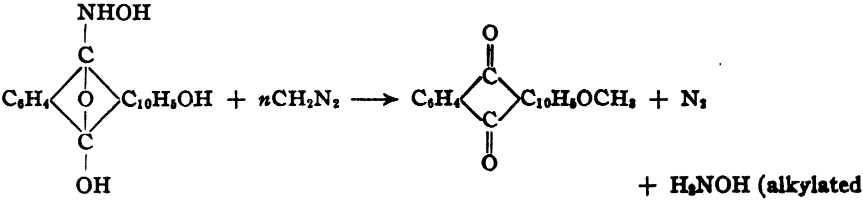
The present observations furnish a clue to the solution of another problem. It was noticed in an earlier investigation[2] that a compound now known to be pleiadenedione (phthaloylnaphthalene) is distinctly more soluble in alcoholic alkali than in alcohol alone. The observation was confirmed by Rieche and his collaborators,[5] who further showed by titration experiments that no true salt is formed and who suggested that the increased solubility was due to the addition of the alkali to a carbonyl group. At a later date various substitution products of the parent diketone were found to show a similar solubility in alcoholic alkali.[3] In the light of the present results, the formation of a definite, if unstable, addition product may be represented as follows



It was stated above that the formation of an oxygen bridge is particularly favored by the spatial configuration of the seven-membered ring which is held in a fixed position between the two aromatic nuclei. In *o*-dibenzoylbenzene a similar configuration can be attained but it represents only one of several possible arrangements, and it is significant that the solubility of this compound in alcohol is not increased by the addition of alkali. This is taken to mean that the formation of the oxygen bridge compounds takes place not only because it is possible, but because the close and fixed proximity of the hydroxyl to the carbonyl group forces an addition to occur.

It is worth noting that the intramolecular addition reaction here pictured is not without analogy, a somewhat similar reaction has been well established in the case of *o*-benzoyl-triphenylcarbinol.[6]

One further reaction of the hydroxylamine addition product is of particular significance on account of the unexpected results encountered in the course of the study. The substance reacts very vigorously with an ethereal solution of diazomethane, and the chief reaction product is the methyl ether of phthaloylnaphthol (X, below). The reaction evidently proceeds thus



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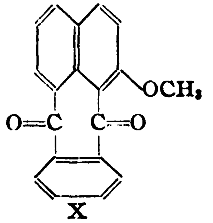
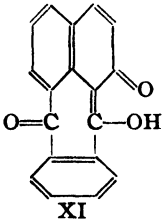
(6) Seidel and Bezner, *Ber.*, **65**, 1566 (1932).

In view of the ease with which hydroxylamine splits off from the molecule in other reactions, it is not surprising that it does so here. What is surprising is that some phthaloylnaphthol was always found in the reaction product, even when a large excess of diazomethane was employed. Indeed the pure hydroxy compound remains unchanged after several hours of contact with an ethereal solution of diazomethane. It might be supposed that the alkylation proceeds in the case noted because the hydroxy compound, normally sparingly soluble in ether, is first brought into solution in the form of the addition product. This, however, cannot be the true explanation, for, although phthaloylnaphthol can be caused to react with diazomethane by using a solution of the diketone in tetrachloroethane, the product formed under these conditions is not identical with the methyl ether (X) formed in the other reaction. It thus appears likely that the breakdown of the hydroxylamine addition compound yields as the immediate product an unstable, tautomeric form of phthaloylnaphthol. Since diazomethane is a reliable reagent for the capture of such an unstable product, and in view of the fact that the structure of the ether formed has been established by synthesis,[3] we are led to the conclusion that the unstable modification has the structure assigned up to the present time to the ordinary, stable form of phthaloylnaphthol. This may be referred to as the naphthol structure.

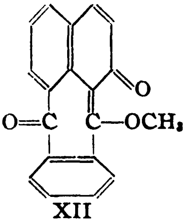
If this reasoning is correct, then ordinary phthaloylnaphthol must have some structure other than that here pictured. The only possibility appears to be the quinonoid structure, XI. It was of considerable interest to study the product of reaction with diazomethane in tetrachloroethane solution, for the structure of this substance might serve to establish the point at issue. The normal reaction product of XI would be the enol ether XII, but this was not the product actually obtained. Instead there was produced a substance having the composition of the starting material plus two methylene groups. Tests and analyses revealed the presence of one methoxyl group, one carbonyl group, and one active hydrogen atom which appears to be enolic. Such a substance might conceivably come from the further reaction of either of the two ethers, X and XII, with a second molecule of diazomethane. The ether of the naphthol form (X), however, was found not to react with diazomethane to the slightest extent in tetrachloroethane solution. The reaction product thus probably results from the addition



X

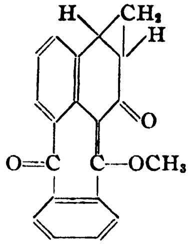


XI

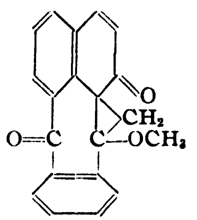


XII

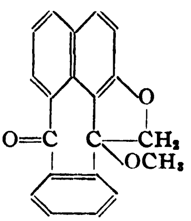
of a methylene group to the ether of the quinoid form, XII. The addition might occur: at the double bond of the quinonoid nucleus to give XIII;



XIII



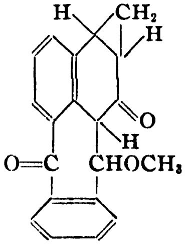
XIV



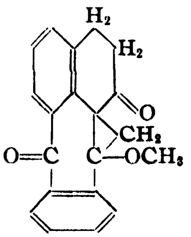
XV

at the double linkage extending to the bridge carbon, forming XIV; or to the ends of the conjugated system, giving XV. Formula XV may be ruled out because it does not indicate a hydrogen atom which can become enolic; the other two formulas are capable of accounting for the properties noted, but it is difficult to distinguish between them.

Several methods of degradation were applied without success, and the only reaction product isolated was that obtained by reduction. The substance was reduced in quantitative yield and in a very few minutes by the action of zinc and acetic acid, forming a nicely crystalline, colorless substance. This is a dihydro derivative of the first compound and contains one methoxyl group. It is not soluble in alkali, but dissolves in alcoholic alkali and is stable toward this reagent, and the Grignard test indicates the presence of one active hydrogen and one carbonyl group. Either XIII or XIV should be capable of easy reduction, and it would be expected that the conjugated system, rather than the cyclopropane ring, would form the point of attack. The reduction product thus might have the structure of either XVI or XVII, and both of these formulas are probably consistent with the properties of the compound.



XVI



XVII

While a distinction between the alternate formulas for the diazomethane reaction product is not yet possible, the facts here presented do make it appear highly probable that phthaloylnaphthol under ordinary conditions possesses the structure of the quinonoid formula XI. There is no reason beyond the argument of probability in support of the hypothesis that the first step in the diazomethane reaction involves the formation of the ether XII, but this point is not essential to the above conclusion. Neither is the problem of the exact structure of the final reaction product; the fact remains that this substance does not come from the naphthol ether X and hence can hardly originate from the naphthol form of phthaloylnaphthol.

There remains for consideration the question as to how well this new conception of structure agrees with the other known reactions of phthaloylnaphthol. One such reaction is that with dimethyl sulfate, which leads to the formation of the naphthol ether, X. The methylation is conducted in an alkaline solution, however, and the composition of the tautomeric equilibrium mixture may be quite different in this medium from the composition in tetrachloroethane solution. Even if it is the quinonoid form which predominates, the formation of the ether isolated would still be possible through a 1,4-addition to the conjugated system. The same may be said of the formation of the primary addition product with hydroxylamine, for this also occurs in an alkaline medium. With these, and with the other known reactions, the new formulation is thus not inconsistent. Whether or not this idea, together with the conception of the formation of the bridge compounds, will aid in the solution of all of the problems connected with the peculiar properties of phthaloylnaphthol is still an open question. We still fail to see any adequate explanation of the course of the oxidation, but in the Grignard reaction it appears probable that the new ideas can be applied to advantage, and this problem will be investigated further.

Experimental Part[7]

1. Oximes of Phthaloylnaphthol

1-Hydroxy-7,12-pleiadenedione-7-oxime (I).—Ten grams of phthaloylnaphthol was dissolved in a mixture of 200 cc. of alcohol and 20 cc. of 6 *N* sodium hydroxide solution and an aqueous solution of 15 g. of hydroxylamine hydrochloride was added to the cold, deep orange-yellow solution. The color changed at once, and the solution became practically colorless and showed only a slight purple fluorescence. On heating under a reflux condenser on the steam-bath the solution soon acquired a yellow color and in about fifteen minutes yellow crystals of the oxime began to separate. After the heating had been continued for two hours, the mixture was cooled and the crystalline product was collected and washed with alcohol; yield, 9 g.; m. p. 242°. The material precipitated from the mother liquor melted at 235°.

The oxime is not appreciably soluble in benzene; it is sparingly soluble in alcohol and moderately soluble in glacial acetic acid. From the latter solvent it crystallizes slowly in the form of small yellow needles melting at 243°.

Anal. Calcd. for $C_{18}H_{11}O_3N$: C, 74.72; H, 3.84. Found: C, 74.35; H, 3.98.

The oxime dissolves in cold alkali and may be recovered unchanged after boiling the yellow solution for several hours. It does not react further with hydroxylamine, even in a strongly alkaline solution. The oxime dissolves in cold concentrated sulfuric acid and the yellow solution becomes deep red when heated, but this apparently does not represent a far-reaching change. Thus the substance was recovered unchanged after being heated for one hour on the steam-bath with 82% sulfuric acid. On heating the red solution at a temperature of 200° for five to ten minutes, however, and pouring the solution onto ice, there was obtained a yellow, alkali-soluble substance melting at 251° which has the composition of the starting material (found: C, 74.60; H, 4.10), and which may be the product of a Beckmann rearrangement.

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[7] The carbon-hydrogen analyses (semi-micro) were carried out by Dr. C. Harold Fisher; Miss Gertrude M. Ware performed the Zeisel determinations (micro).

The diacetate of the oxime crystallizes from glacial acetic acid as pale yellow prisms melting at 237°.

Anal. Calcd. for $C_{22}H_{15}O_6N$: C, 70.76; H, 4.05. Found: C, 70.77; H, 4.25.

The oxime was converted into a **dehydro product, probably IV,** by the action of heat. When the oxime is melted in a capillary tube, the formation of gas bubbles is observed at a temperature only a few degrees above the melting point. A quantity of the material was heated in a metal bath under vacuum at 300–320° until the reaction was complete and the residue was then distilled and crystallized from glacial acetic acid. There was thus obtained a substance melting sharply at 260° and forming long, slender, orange-yellow needles. It is insoluble in aqueous sodium hydroxide solution, but dissolves in hot alcoholic alkali solution. The solution shows no change on heating, and the compound may also be recovered after short heating with concentrated sulfuric acid.

Anal. Calcd. for $C_{18}H_9O_3N$: C, 75.25; H, 3.16. Found: C, 75.19; H, 3.25.

The presence of a single hydroxyl group is indicated by the formation of a **monoacetate.** This forms small, pale yellow needles melting at 208° from benzene–ligroin.

Anal. Calcd. for $C_{20}H_{11}O_4N$: C, 72.93; H, 3.37. Found: C, 73.05; H, 3.39.

The isomeric **anhydro compounds of 1,6-dihydroxypleiadenedione oxime, V,** was prepared by heating a solution of this diketone[6] in aqueous alkali with hydroxylamine for several hours. The reaction product is but sparingly soluble in alkali and thus separates from the hot solution as it is formed. It crystallizes well from glacial acetic acid, forming long, yellow needles melting at 292°. The compound is not identical with the above substance of melting point 260°, but resembles it in the stability to the action of acids and alkalies and in being soluble in alcoholic alkali.

Anal. Calcd. for $C_{18}H_9O_3N$: C, 75.25; H, 3.16. Found: C, 75.04; H, 3.42.

1-Hydroxy-7,12-pleiadenedione-12-oxime (II).—The 12-oxime is formed along with the 7-oxime in the reaction of phthaloylnaphthol with hydroxylamine in alcoholic alkaline solution if the amount of alkali present is much greater than that specified above. Following the procedure given, but using twice the quantity of alkali, the yield of the 7-oxime was about 10% lower and a small quantity of the 12-isomer was isolated from the mother liquor. With a four-fold quantity of alkali (80 cc. of 6 *N* sodium hydroxide solution for a 10-g. sample), no crystals of the 7-oxime separated even on cooling the reaction mixture, but the solution was found to contain some of this substance along with a larger quantity of the 12-oxime. The latter compound was isolated in a fairly good condition by carefully adding water and acid until about one-third of the material present had been precipitated. The 7-oxime was carried into the precipitate, and the isomer then could be precipitated from the mother liquor.

A somewhat surer method of preparing a sample of the 12-oxime which is free from traces of the isomer was found in the hydrolysis of the acetate prepared, as described below, from the hydroxylamine addition product.

The oxime in question does not crystallize well from any of the usual solvents. The best samples were obtained by precipitating the material from a solution in pyridine by means of alcohol, and then by acidifying and gradually diluting a solution of the material in cold alcoholic alkali. The product separated slowly as a yellow, microcrystalline powder. It melts fairly sharply at 262° with loss of water and conversion into the anhydro compound (see below).

Anal. Calcd. for $C_{18}H_{11}O_3N$: C, 74.72; H, 3.84. Found: C, 74.07; H, 3.96.

The oxime appears to be fairly stable in an alcoholic solution containing alkali, even at the boiling point, but in an aqueous solution of alkali it is converted rapidly into the anhydro compound, which precipitates as it is formed. The same substance is the chief product obtained by the action of acetic anhydride on the oxime, even in the presence of sodium acetate. The oxime is also dehydrated by the action of hot, 82% sulfuric acid.

The best method found for the preparation of the **12-oxime diacetate** consists in the use of pyridine as catalyst. A solution of the oxime in pyridine was cooled in an ice-bath and treated with acetic anhydride. After one-half hour in the ice-bath, the solution was allowed to stand at room temperature for several hours (heating the solution causes the anhydro compound to form) and it was then poured into water. The crude product melted at 155–160°, and it was only after several crystallizations from alcohol that a homogeneous substance was obtained. This formed small, pale yellow crystals melting at 174°. It is converted into the oxime on hydrolysis with alcoholic alkali and yields the anhydro compound when heated with sulfuric acid.

Anal. Calcd. for $C_{22}H_{15}O_5N$: C, 70.76; H, 4.05. Found: C, 71.15; H, 4.15.

The anhydro compound, III, of the 12-oxime was obtained in a variety of ways which for the most part have been indicated already. The loss of a molecule of water from the oxime takes place easily in an aqueous solution of sodium hydroxide, while the reaction is arrested by the presence of a considerable quantity of alcohol. Thus the substance may be prepared directly from phthaloylnaphthol by heating 1 g. of this substance with 50 cc. of water, 4 cc. of 6 *N* sodium hydroxide solution and 1.5 g. of hydroxylamine hydrochloride; a small quantity of the 7-oxime was isolated from the mother liquor. The anhydro compound was also obtained in nearly quantitative yield by boiling for two hours a mixture of 1 g. of phthaloylnaphthol methyl ether, 30 cc. of alcohol, 8 cc. of 6 *N* alkali and 1.5 g. of hydroxylamine hydrochloride. The product separated in a crystalline condition from the boiling solution. The compound is moderately soluble in glacial acetic acid and crystallizes in the form of very long, colorless needles melting at 227°. It is not soluble in alkali or in alcoholic alkali, and it was recovered unchanged after boiling a solution of the material in 82% sulfuric acid.

Anal. Calcd. for $C_{18}H_9O_2N$: C, 79.69; H, 3.35. Found: C, 79.41; H, 3.43.

2. Phthaloylnaphthol–Hydroxylamine Addition Product

One gram of pure phthaloylnaphthol was dissolved by heating in a mixture of 30 cc. of water and 2 cc. of 6 *N* sodium hydroxide solution and the orange yellow solution was cooled and filtered. A cold solution of 1 g. of hydroxylamine in water was then added in small portions. The first few drops caused the precipitation of the yellow starting material, which redissolved on shaking, and then the color of the solution changed from deep orange-yellow to a very pale yellow with a faint purple fluorescence. This point was reached when approximately one equivalent of the reagent had been added. With the addition of the remainder of the amine salt the solution became weakly acidic and a white precipitate having a definite microcrystalline structure soon separated. This was collected, washed thoroughly with water, and dried in a vacuum desiccator over potassium hydroxide. The material on drying retained the crystalline character but acquired a pale yellow color. A sample which had been dried for two days gave the following analytical figures.

Anal. Calcd. for $C_{18}H_{13}O_4N$: C, 70.34; H, 4.26. Found: C, 70.11; H, 4.39.

The freshly-precipitated, colorless material may be a hydrate; except for the fact that it contains external moisture, it behaves exactly like the dried material. The yellow, dried material decomposes at about 135° and yields a mixture containing phthaloylnaphthol and its oximes or their further reaction products. It undergoes slow decomposition even at room temperature and cannot be preserved for more than a few days. The addition product dissolves much more readily than phthaloylnaphthol in organic solvents and in alkali. It dissolves easily in cold alcohol to give a nearly colorless solution. This becomes yellow on standing, or on being heated, and phthaloylnaphthol soon precipitates. The reversion to the starting material is catalyzed by acids, the change taking place at once when the addition product is dissolved in glacial acetic acid, or when a small quantity of this acid is added to a cold solution of the material in alcohol or ether.

The addition product is not soluble in sodium carbonate solution but it dissolves readily in cold alkali. The solution is at first nearly colorless, but on warming it acquires at once the orange-yellow color characteristic of the salt of phthaloylnaphthol. This substance can be isolated from the solution if the heating is interrupted as soon as the color change is complete. When the heating is continued for several hours there is produced a mixture of the 7-oxime and the anhydro derivative of the 12-oxime. These products obviously are not formed directly from the addition product, but are formed from the interaction of its component parts. The same result is obtained on starting with phthaloylnaphthol, hydroxylamine and aqueous alkali.

While the addition product could not be converted directly into an oxime without a preliminary breakdown of the molecule, it was found possible to convert the substance into an oxime diacetate under suitable conditions. With acetic anhydride alone, or in combination with either sodium acetate or sulfuric acid, the addition compound is converted chiefly into phthaloylnaphthol acetate. This acetate was also produced to a certain extent in pyridine solution, but there was also formed a considerable quantity of a **diacetate of the 12-oxime.** One gram of the dry addition product was dissolved in 10 cc. of cold pyridine and 4 cc. of acetic anhydride was added to the pale yellow solution. The mixture became warm and after standing for one hour it was poured into water and the precipitate was crystallized repeatedly from alcohol. The small amount of phthaloylnaphthol acetate usually present is less soluble than the main reaction product and is thus removed only with difficulty. The oxime diacetate, however, was obtained in an apparently pure condition from the more soluble fractions. It forms faintly yellow needles melting at 163°.

Anal. Calcd. for $C_{22}H_{15}O_5N$: C, 70.76; H, 4.05. Found: C, 70.61; H, 4.23.

The diacetate is hydrolyzed easily by alcoholic alkali and too drastic treatment leads to the formation of the anhydro derivative of the oxime. Suspended in cold alcoholic alkali, it soon passed into solution and no precipitate formed on dilution with water. On acidification there slowly separated in quantitative yield a yellow substance melting at 262° and found to be identical with the 12-oxime. No trace of the 7-oxime was found on hydrolysis of either the pure or the crude diacetate. This is in contrast to the result obtained on heating for several hours a solution of the addition product in pyridine: both the 7- and the 12-oxime were isolated from the reaction mixture.

The oxime diacetate, m. p. 163°, here described appears to be different from the diacetate, m. p. 174°, obtained directly from the 12-oxime, though they both yield the same substance on hydrolysis. Mixtures of the two diacetates melted at about 154–157°. It is possible that they are stereoisomers, and it is also possible that the lower melting compound is present in the reaction mixture obtained on acetylation of the 12-oxime, for the higher melting diacetate was isolated in a pure condition only after several crystallizations.

The hydroxylamine addition product was treated with an ethereal solution of diazomethane (containing some methyl alcohol) both in the dry condition (yellow) and when freshly precipitated (white). In each case there was a vigorous evolution of nitrogen and the odor of alkylated hydroxylamine was apparent. The ether was evaporated and the oily residue was converted to a solid by digestion with alcohol. A rather considerable quantity of phthaloylnaphthol was eliminated by digestion with alkali, and the product was then crystallized from glacial acetic acid. Well-formed, yellow crystals melting at 205° were obtained, and the substance was found identical, by mixed melting point determinations, with the methyl ether of phthaloylnaphthol.

The Action of Other Amines.—Since the formation of the hydroxylamine addition product is accompanied by a marked color change, it was a simple matter to determine if derivatives of this amine and other similar compounds are capable of forming addition products with phthaloylnaphthol. The tests were negative with the following compounds: N-methylhydroxylamine, phenylhydrazine, diphenylhydrazine, semicarbazide and nitroxyl (from benzenesulfohydroxamic acid). The solution remained yellow and the starting material was recovered unchanged.

Hydrazine itself was the only other compound found to enter into reaction.

A solution of 1 g. of phthaloylnaphthol in 30 cc. of hot water and 4 cc. of 6 *N* alkali was cooled, and to the suspension of the sodium salt thus formed there was added in portions a solution of 2 g. of hydrazine hydrochloride. The sodium salt dissolved, a pale yellow solution with a purple fluorescence was produced, and then a faintly yellow addition product was precipitated. It did not have as good a crystalline character as the other addition product and it could not be obtained in a form suitable for analysis. Like the other product, the substance dissolves in alkali or in alcohol to give faintly yellow solutions which became deep yellow on heating. It also dissolves in dilute hydrochloric acid, but phthaloylnaphthol begins to separate even before the dissolution is complete. The addition product was converted by acetylation in a cold pyridine solution into a substance having the composition of the **hydrazone diacetate.** The compound crystallizes from alcohol in the form of small, faintly yellow crystals melting at 199–200°.

Anal. Calcd. for $C_{22}H_{16}O_4N_2$: C, 70.95; H, 4.33. Found: C, 70.77; H, 4.60.

3. The Action of Diazomethane on Phthaloylnaphthol

Even in a finely divided condition, phthaloylnaphthol is not appreciably affected by prolonged contact with an ethereal solution of diazomethane. When, however, the material is brought into solution in a suitable solvent a fairly rapid reaction occurs. No difference was noticed in the action of diazomethane in an absolute ethereal solution and in a solution containing some methyl alcohol and water. The yield was never quantitative and there was always an intractable, resinous residue. On using only a small fraction of the diazomethane specified below, the only change was that a considerable quantity of starting material was recovered unaltered.

To a cold solution of 7 g. of phthaloylnaphthol in 180 cc. of tetrachloroethane there was added an ethereal solution of diazomethane prepared either from 10.4 cc. of nitrosomethylurethan or from 10 g. of nitrosomethylurea. A steady, if not vigorous, reaction became apparent and continued for about two hours. After standing for two to three hours longer, the ether was evaporated and the remaining solvent removed by steam distillation. An oily residue adhered to the flask and the water could be removed from this by decantation. Sufficient alcohol was added to dissolve the oil and the solution on cooling deposited good crystals of the nearly pure reaction product; yield, 2.8–3.1 g. On evaporation of the mother liquor, trituration of the glassy residue with glacial acetic acid or with alcohol, and repeated crystallization of the product, there was obtained about 0.1 g. of a second substance, melting at 205° and identified as phthaloylnaphthol methyl ether. In separate experiments it was established that this ether does not react with diazomethane in tetrachloroethane solution.

The diazomethane reaction product (XIII or XIV) dissolves readily in glacial acetic acid or in benzene and is moderately soluble in alcohol. It crystallizes from alcohol or from benzene-ligroin as small, faintly yellow needles melting at 208°. It is not soluble in alkali and forms in concentrated sulfuric acid a deep red-purple solution which turns brown on heating. A suspension of the finely divided material in cold alcohol dissolves slowly on adding a few drops of alkali solution and shaking the mixture. It is easily oxidized and it reacts with hydrogen bromide in glacial acetic acid solution, but a clean reaction product was not isolated in either case. In a quantitative test with the Grignard reagent, using as solvent a mixture of diphenyl ether and xylene,[8] 1 mole of substance was found to yield 1.2 moles of gas and to consume (total) 2.14 moles of reagent. The solution of the reactants had a brilliant red color.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67; OCH_3, 10.26. Found: C, 79.25, 79.07; H, 4.70, 4.67; OCH_3, 10.24, 10.40.

A reduction product (XVI or XVII) was obtained as follows. Two grams of the above material was dissolved in 50 cc. of glacial acetic acid and the solution was boiled under reflux for ten minutes with 5 g. of zinc dust. The yellow color of the original solution disappeared in about five minutes. The combined filtrate and washings from the zinc were treated with water, which precipitated a nearly colorless solid melting at 243°; yield, 1.9 g. The compound is only moderately soluble in alcohol and crystallizes slowly from this solvent as well-formed, colorless prisms melting at 245°.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.92; H, 5.30; OCH_3, 10.20. Found: C, 78.79; H, 5.31; OCH_3, 10.49, 10.17.

The compound is not soluble in alkali but dissolves in alcoholic alkali, precipitating from the solution on dilution with water. The material was recovered unchanged after boiling for three hours a solution in alcoholic alkali. In diphenyl ether-xylene solution 1 mole of the substance liberated 1.16 mole of gas and consumed (total 2.02 moles of Grignard reagent. The reduction product forms in concentrated sulfuric acid an intensely colored solution with a blue-purple fluorescence.

The acetate of the reduction product crystallizes from alcohol in the form of clusters of colorless plates, m. p. 184°.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 75.99, 75.78; H, 4.68, 5.13.

A further substance obtained only in small quantity and not identified was prepared by boiling a suspension of the reduction product in benzene with aluminum chloride. The mixture became intensely green and an oily green substance separated. In five minutes this had all dissolved to give a deep red solution. On working up the mixture there was obtained a substance forming yellow needles, m. p. 257°, and soluble in hot alkali.

Summary

Phthaloylnaphthol forms with hydroxylamine an unstable addition product which can be converted into an oxime derivative by loss of water. This remarkable reaction is attributed not to an unusual reactivity of the carbonyl group but to a secondary stabilization involving an addition to the second carbonyl group.

The reaction of phthaloylnaphthol with diazomethane furnishes certain indications that the compound in question exists largely in a tautomeric, quinonoid form.

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CAMBRIDGE, MASSACHUSETTS

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[8] Schmitz-Dumont and Hamann, *Ber.*, **66**, 71 (1933).

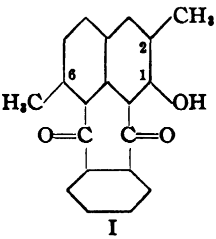
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Some Further Derivatives of Pleiadene[1]

BY LOUIS F. FIESER

This paper includes an account of the preparation of certain compounds required in connection with the study of the action of hydroxylamine and of diazomethane on phthaloylnaphthol,[2] and describes also some synthetical experiments carried out in an attempt to extend the observations already recorded.

The diketone I was prepared partly in order to determine if it forms a hydroxylamine addition product, which it does, and partly with the idea that the methyl group at position 2 might block a possible addition of diazomethane to the double bond of the quinonoid form. While this indeed may be the case, the compound proved to be of little use because it does not even form an ether on treatment with the reagent in question. The hydroxyl group appears to be masked, for the compound, unlike phthaloylnaphthol, does not dissolve in aqueous alkali. The same inert character is shown by a compound of similar structural type obtained by the condensation of phthalic anhydride with 2-phenanthrol (No. 2, Table I, below), and it would thus appear that this line of attack is not profitable.



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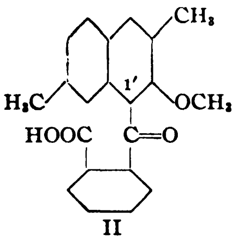

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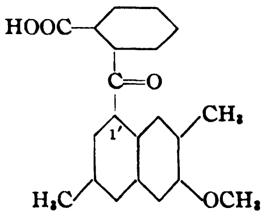

III

The dimethyl derivative I was prepared by heating a mixture of phthalic anhydride, 2,6-dimethyl-7-naphthol[3] and aluminum chloride to a temperature of 200°, and yet the product was obtained in so excellent a yield and in such a high state of purity that it does not appear likely that there was any wandering of methyl groups in the course of the reaction. We sought to establish the point by the stepwise synthesis of the diketone, but unforeseen difficulties were encountered. In the first place the Friedel and Crafts reaction of phthalic anhydride with 2,6-dimethyl-7-methoxynaphthalene proceeded very poorly, a large proportion of the ether being recovered unchanged. More serious, however, was the fact that the chief reaction product was not the expected keto acid, II, desired for the synthesis, but an isomeric acid probably having the structure of III. The acid forms an anthraquinone on treatment with sulfuric acid and hence the keto group

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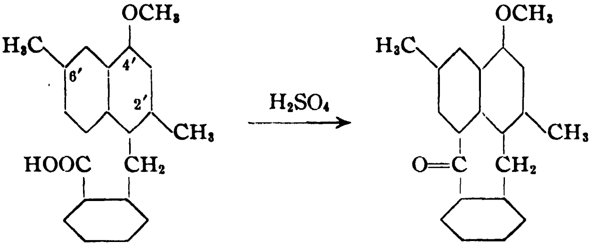
(1) Eighth paper in the series, "Condensations and Ring Closures in the Naphthalene Series."

(2) Seventh paper, THIS JOURNAL, 55, 4963 (1933).

(3) Weissgerber and Kruber, *Ber.*, 52, 346 (1919).

must be situated at either the 1′ (α) position, as here pictured, or at the 2′ (β) position. A keto acid which is incapable of undergoing ring closure to form an anthraquinone, and which probably has the structure of II, was also found in the reaction mixture but in quantity too small for the purpose at hand.

In another series of experiments an attempt was made to synthesize a substance similar to phthaloylnaphthol but having the hydroxyl group in the para rather than the ortho position with respect to a carbonyl group, for such a compound should prove an interesting subject for study. 2,6-Dimethyl-8-methoxynaphthalene was chosen as the most accessible starting material, and it was found to condense with phthalic anhydride in the 4-position as expected, though in poor yield. The keto acid failed to undergo cyclization on treatment with sulfuric acid, while its reduction product, IV, was easily converted into the ketone, V. These facts are sufficient to establish the structures of the compounds in question. It is worth noting that the cyclization of IV can be accomplished by heating the substance with sulfuric acid. The yield is quantitative and the closing of the 7-membered ring occurs just as easily as the closing of an anthrone 6-ring from an acid in which such a reaction is not blocked by a substituent group. The pleiadone derivative, however, although obtainable without great difficulty, could not be converted by oxidation into a pleiadenedione. Though disappointing, the failure of this attempted synthesis was not a great surprise, for the presence of a methoxyl group has been found to introduce complications in other oxidations of the same type.[4]



IV V

The theoretical significance of obtaining for study a pleiadone derivative in which the carbonyl group is adjacent to a hydroxyl group has been discussed in the preceding paper.[2] In a first attempt to prepare such a compound, phthaloylnaphthol was reduced by high pressure hydrogenation, and the reduction product, in the form of the acetate (VI), was subjected to partial oxidation. The oxidation product, however, was the known ketone, VII,[4] rather than the desired isomer. This method failing, we obtained a compound of the desired type from the acid VIII, which was prepared by the usual synthesis, starting with 2,7-dimethoxynaphthalene.

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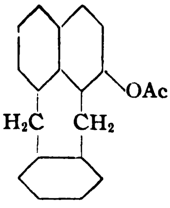
(4) L. F. and M. Fieser, THIS JOURNAL, 55, 3010 (1933).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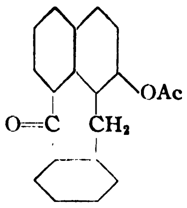
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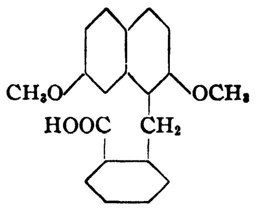
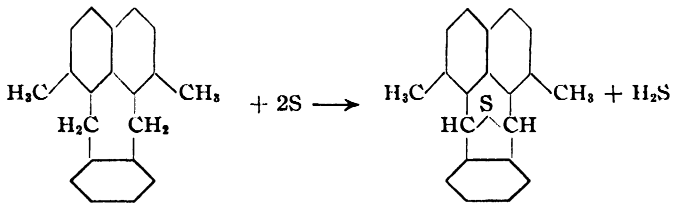

VIII

The closing of the 7-ring was again brought about in a very satisfactory manner by the action of sulfuric acid on VIII, and the resulting ketone on demethylation yielded 1,6-dihydroxypleiadone.

In connection with this miscellany of compounds and experiments, we may report the results of a brief study of the possibility of producing a true pleiadene by the dehydrogenation of the corresponding dihydropleiadene. The dimethyl compound IX gave no clean products on reaction with selenium, but was converted by the action of sulfur into a quite stable and a nicely crystalline compound containing sulfur and having two atoms of hydrogen less than the starting material. Without being able at this time to present any but analytical evidence in support of the view, we may offer the following equation as representing the most probable course of the reaction


IX X

The production of the sulfur bridge may be preceded by the formation of the unsaturated hydrocarbon by dehydrogenation, and if this is the case the pleiadene is distinctly more reactive than the similarly constituted hydrocarbon anthracene.

The possibility of dehydrogenating the hydrocarbon IX with bromine was also studied and with equally surprising results. In glacial acetic acid solution the hydrocarbon combines with bromine according to the equation: $C_{20}H_{18} + CH_3COOH + Br_2 = C_{20}H_{17}Br\cdot CH_3COOH + HBr$. The reaction product is crystalline, but unstable to heat, and when treated with cold pyridine it is converted into a stable bromo compound, $C_{20}H_{17}Br$. The first product is not a molecular compound derived from the second substance, for the latter crystallizes from glacial acetic acid without solvation. The primary reaction product loses some hydrogen bromide on heating, along with acetic acid, whereas the second substance is not attacked by alcoholic alkali. From these facts it is concluded that bromine first attacks a methylene or a methyl group to form a substance which combines, probably with the formation of a molecular compound, with acetic acid. Pyridine causes both the elimination of the acetic acid and the rearrangement to a nuclear bromo derivative.

Experimental Part[5]

1. Pleiadenediones

The compounds listed in Table I as Nos. 1, 2 and 4 were prepared by adding 1 part of 2,3-dihydroxynaphthalene, 2-phenanthrol or 2,6-dimethyl-7-naphthol,[3] respectively, to a melt from 10 parts of phthalic anhydride and 2 parts of aluminum chloride at a temperature of 160–170°. The temperature was raised to 200° and held there, with good stirring, for one-half hour, when the melt was poured into boiling water. The yellow precipitate was digested with boiling water, crystallized from glacial acetic acid, distilled, and again crystallized. The yield in the first case was only 32% of the theoretical amount; the other two compounds were obtained in yields of 85–90%. As would be expected, Compound 1 dissolves easily in cold alkali; the other two compounds are not appreciably soluble in boiling aqueous sodium hydroxide solution but dissolve easily in alcoholic alkali. These solutions in alkali or alcoholic alkali are deep orange-yellow in color and the addition of hydroxylamine hydrochloride causes first a striking change to a nearly colorless solution and then the separation of a colorless product having all the characteristics of the addition product of phthaloylnaphthol. The action of diazomethane in tetrachloroethane solution on the two alkali-insoluble compounds, Nos. 2 and 4, was studied repeatedly, but no product other than the unchanged starting material could be isolated.

TABLE I

DERIVATIVES OF 7,12-PLEIADENEDIONE

No.	Substituents	Description	M. p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	1,2-Dihydroxy	Yellow needles	233	74.47	74.09	3.47	3.84
2	1-Hydroxy-4,5-benz	Yellow needles	240	81.47	81.54	3.73	3.86
3	Acetate of No. 2	Pale yellow	227	78.67	78.17	3.85	3.85
4 (I)[6]	2,6-Dimethyl-1-hydroxy	Yellow needles	209	79.45	79.41	4.67	4.54
5	Acetate of No. 4	Pale yellow	205	76.72	76.52	4.69	4.73

In an attempt to establish by synthesis the structure of the hydroxydimethyl diketone, No. 4, phthalic anhydride was condensed with 2,6-dimethyl-7-methoxynaphthalene in tetrachloroethane solution in the presence of aluminum chloride. The mixture was cooled in a salt-ice bath and stirred intermittently for three days. In spite of the long period allowed for reaction, about half of the ether was recovered unchanged.

The soda-soluble portion consisted in predominant amount of a keto acid melting at 212° and convertible into an anthraquinone, and there was only a very small amount of the keto acid (m. p. 223°) desired for the synthesis indicated. The lower-melting isomer was isolated by crystallization from toluene and further purified by recrystallization from alcohol, in which, however, it is quite soluble. The other isomer is considerably less soluble in this solvent, and it was obtained in a pure condition by extracting the residue recovered from the toluene solution with alcohol to remove the needles of the isomer, m. p. 212°, and crystallizing the residue from the same solvent.

The conversion of the lower-melting keto acid into a quinone was accomplished by

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(5) I am indebted to Dr. C. Harold Fisher for the analyses here reported and to Mrs. Louis F. Fieser for assistance in the preparative work.

(6) The Roman numeral refers to the formula given above.

heating the material (1 g.) with 82% sulfuric acid (10 cc.) for one-half hour on the steam-bath. The quinone began to separate from the red solution even before all of the acid had dissolved. The anthraquinone derivative was recognized as such from the characteristic red vat which is formed. The compounds here mentioned are described in Table II.

TABLE II

COMPOUNDS OBTAINED FROM 2,6-DIMETHYL-7-HYDROXYNAPHTHALENE

Name	Description	Color in H_2SO_4	M. p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2,6-Dimethyl-7-methoxy-naphthalene	Plates	None	82	83.82	84.33	7.58	7.43
3′,7-Dimethyl-6′-methoxy-1′ (or 2′)-naphthoyl-2-benzoic acid (III?)	Colorless needles	Red-purple	212	75.42	75.22	5.43	5.52
2′,4-Dimethyl-3′-methoxy-1,2-benzanthraquinone	Yellow needles	Purple	235	79.72	79.66	5.10	5.13
3′,7′-Dimethyl-2′-methoxy-1′-naphthoyl-2-benzoic acid (II?)	Yellow prisms	Blue-green	223	75.42	75.41	5.43	5.64

2. Pleiadones

The starting materials required for the synthesis of the cyclic monoketones were 2,7-dimethoxynaphthalene and 2,6-dimethyl-8-methoxynaphthalene. Two acids may be obtained by the sulfonation of 2,6-dimethylnaphthalene under suitable conditions[3] and these yield on fusion with alkali the naphthol desired and that utilized in experiments described in Section 1. In separating the acids and determining their purity it was found useful to know the melting points of the *p*-toluidine salts. These are as follows: 2,6-dimethylnaphthalene-8-sulfonate, 279°; 2,6-dimethylnaphthalene-7-sulfonate, 286°.

2,6-Dimethyl-8-methoxynaphthalene was prepared from the naphthol by methylation with dimethyl sulfate in a hot, alkaline solution. The product was distilled and then crystallized from methyl alcohol; colorless plates, m. p. 58°.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.82; H, 7.59. Found: C, 83.66; H, 7.53.

The compounds obtained from the condensation of this ether and of the dimethoxynaphthalene with phthalic anhydride and in the subsequent reductions and ring closures are listed in Table III.

TABLE III

PROPERTIES AND ANALYSES OF COMPOUNDS

No.	Substituents	Description	M. p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
		1′-Naphthoyl-2-benzoic acids					
6	2′,7′-$(OCH_3)_2$	Colorless plates	201	71.41	71.37	4.80	4.79
7	2′,6′-$(CH_3)_2$-4′-(OCH_3)	Yellow needles	261	75.42	75.38	5.43	5.47
		1′-Naphthoyl-2-benzoic acid methyl ester					
8	2′,7′-$(OCH_3)_2$	Prisms	114	71.98	71.95	5.18	5.33
		1′-Naphthylmethyl-2-benzoic acids					
9(VIII)	2′,7′-$(OCH_3)_2$	Fibrous needles	161	74.51	73.98	5.63	5.52
10(IV)	2′,6′-$(CH_3)_2$-4′-(OCH_3)	Colorless needles	236	78.72	78.37	6.30	6.39
		12-Pleiadones					
11	1,6-$(OCH_3)_2$	Yellow needles	201	78.92	78.99	5.30	5.13
12	1,6-$(OH)_2$	Yellow needles	233	78.24	78.09	4.38	4.26
13	1,6-$(OAc)_2$	Colorless plates	220	73.31	72.76	4.48	4.39
14(V)	2,6-$(CH_3)_2$-4-(OCH_3)	Bright yel. needles	241	83.41	82.98	6.00	6.14
15	2,6-$(CH_3)_2$-4-(OH)	Bright yel. needles	286	83.30	83.17	5.60	5.55

The Friedel and Crafts reaction with 2,7-dimethoxynaphthalene was carried out at −15° in tetrachloroethane solution for twenty hours, and about one-third of the ether was recovered unchanged. The keto acid, No. 6, was purified through the methyl ester and then by crystallization of the sodium salt. This salt crystallizes well from water, but not in the presence of alcohol. The keto acid (20 g.) was reduced with zinc dust (35 g.) in alkaline solution (25 g. of sodium hydroxide in 300 cc. of water), the mixture being boiled for two hours and heated overnight on the steam-bath. The acid, Compound No. 9, was precipitated twice as the sodium salt with alkali and sodium chloride and then crystallized from benzene–ligroin; yield, 17.5 g.

The closure of the 7-membered ring to give the pleiadone, No. 11, was accomplished most easily by the action of sulfuric acid. The product was cleaner and the yield just as good as when the acid chloride was treated with aluminum chloride in nitrobenzene solution. Thus 1 g. of the acid was stirred into 10 cc. of 82% sulfuric acid (green-yellow fluorescence) and the mixture was heated on the steam-bath for twenty minutes, when a deep red solution was obtained. The reaction product, precipitated by water and digested with soda solution, was practically pure; yield, 0.9 g. The substance crystallizes well from alcohol.

Demethylation was accomplished by boiling for three hours a solution of 4 g. of the ether in benzene with 10 g. of aluminum chloride. The benzene was removed by steam distillation and the dihydroxypleiadone (No. 12) was obtained in a nearly pure condition and in quantitative yield after being precipitated from a solution in alkali. The compound crystallizes well from alcohol. The yellow solution in alkali does not change in color on the addition of hydroxylamine and there is thus no indication of the formation of an addition product.

The condensation of phthalic anhydride with 2,6-dimethyl-8-methoxynaphthalene did not proceed well under any of the conditions tried. Both tetrachloroethane and nitrobenzene were used as solvent and the reaction was run at −15° and at room temperature and for varying periods of time (up to three days). In every case a considerable quantity of the starting material was recovered unchanged. The reaction mixture, however, appeared to contain only one keto acid, No. 7. To isolate this the oily solid left as a residue after steam distillation of the solvent was digested with alcohol. This dissolved the ether and left a solid residue of the acid, which was easily purified by crystallization from glacial acetic acid (moderately soluble). The acid forms a very sparingly soluble sodium salt. On this account it was found advisable to carry out the reduction with zinc and alkali in an alcoholic rather than an aqueous solution. Thus a mixture of 10 g. of the keto acid, 25 cc. of 6 N sodium hydroxide, 125 cc. of alcohol and 25 g. of zinc dust was boiled under the reflux condenser for two days, with the addition of 50 cc. of alkali solution and 25 g. of zinc at intervals. An equal volume of water was added, the bulk of the alcohol was removed by distillation and the solution was filtered and acidified. After precipitating the acid (No. 10) from a soda solution and digesting the material at the boiling point, there was obtained 9.3 g. of the nearly pure acid which required a single crystallization from alcohol.

The ring closure to the monoketone (No. 14) was again accomplished with the use of sulfuric acid, 1 g. of the acid being warmed for ten minutes on the steam-bath with 1 cc. of water and 8 cc. of concd. sulfuric acid. The solution became green for a moment and soon changed in color to an intense blue. The ketone, precipitated with water and digested with a small amount of alcohol, in which it is sparingly soluble, was obtained directly in a nearly pure condition; yield, 0.9 g. The compound crystallizes well from glacial acetic acid; the solution in concd. sulfuric acid is purple. Demethylation with aluminum chloride proceeded smoothly and the hydroxy compound, No. 15, crystallized well from glacial acetic acid. The compound dissolves in hot alkali to give a red solution; when in a finely divided condition it dissolves slowly in the cold. Hydroxylamine forms no additive compound in alkaline solution. Attempts to oxidize the methylene group of the ether, No. 14, with either chromic acid or selenious acid were unsuccessful.

3. Dihydropleiadenes

1-Hydroxy-7,12-dihydropleiadene.—This compound was prepared by the hydrogenation of phthaloylnaphthol in the pressure apparatus described by Adkins and Connor.[7] Using 15 g. of material suspended in 150 cc. of alcohol and 3 g. of copper chromite catalyst,[8] the reaction proceeded rapidly at a moderate pressure and at a temperature of 155°; yield, 7.3 g. The substance is very soluble in alcohol or benzene and crystallizes well from benzene–ligroin as clusters of colorless, fibrous needles melting at 179°. It dissolves easily in cold alkali and the solution exhibits a distinct violet fluorescence.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 87.77; H, 5.73. Found: C, 87.69; H, 5.71.

The acetate (VI), crystallized from alcohol, forms long, fine needles melting at 136°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.30; H, 5.60. Found: C, 83.76; H, 5.71.

The acetate was converted by oxidation with chromic acid in glacial acetic acid solution to a substance, m. p. 195°, identified as 1-acetoxy-7-pleiadone;[4] yield, 30%.

1,6-Dimethyl-7,12-dihydropleiadene (IX).—1,6-Dimethylpleiadone[4] was hydrogenated easily in the pressure bomb under the conditions described above; yield, 60%. The compound is moderately soluble in alcohol and crystallizes from this solvent in colorless needles which may grow to a length of 10–12 cm. The solution has a purple fluorescence. On warming the compound with concd. sulfuric acid a cherry-red coloration is produced. The melting point is 133°.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.74; H, 7.05.

Attempts to nitrate the hydrocarbon led only to oily, yellow mixtures largely soluble in alcoholic alkali. Selenium had little effect on the hydrocarbon at 350° and at higher temperatures hard, insoluble solids were produced.

The Action of Sulfur (X?).—A mixture of 3 g. of the hydrocarbon and 1 g. of sulfur was heated in a small distilling flask in a metal bath and the temperature was raised rapidly. The evolution of hydrogen sulfide began at 200° and became very rapid at 260°. After heating at this temperature for eight minutes, the product was distilled *in vacuo*, a considerable black residue being left in the flask. The distillate solidified on rubbing it with alcohol. It was redistilled and then crystallized from glacial acetic acid until pure; yield, 1 g. The compound is very readily soluble in benzene, moderately soluble in glacial acetic acid or ligroin, sparingly soluble in alcohol. From glacial acetic acid it separates very slowly in the form of large, rectangular, pale orange prisms melting at 217°. It forms a deep red solution in concd. sulfuric acid. The compound contains sulfur.

Anal. Calcd. for $C_{20}H_{16}S$: C, 83.28; H, 5.60. Found: C, 83.17; H, 5.84.

The Action of Bromine.—A solution of 2.6 g. of the hydrocarbon in 40 cc. of glacial acetic acid was cooled to 80° and treated with a solution of 1.8 g. of bromine in a little glacial acetic acid. The bromine was taken up at once and hydrogen bromide was evolved. The solution on cooling deposited 2.5 g. of thick, dull yellow needles. No good product was obtained from the mother liquor. The material collected decomposes on heating at 150–160°, and it darkens when heated in glacial acetic acid solution. No solvent was found suitable for a crystallization. The crude material, however, being stable at room temperature, appeared suitable for analysis.

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(7) Adkins and Connor, THIS JOURNAL, 53, 1091 (1931).

(8) Catalyst "37 K A F" of Connor, Folkers and Adkins, *ibid.*, 54, 1140 (1932).

Anal. Calcd. for $C_{22}H_{21}O_2Br$: C, 66.49; H, 5.33. Found: C, 66.46, 66.67; H, 4.76, 4.66.

The second compound, a **bromo-1,6-dimethyldihydropleiadene,** was best prepared as follows: 1 g. of the primary bromination product was shaken in the cold with 4 cc. of pyridine for one-half hour. The needles gradually disappeared and when dissolution was nearly complete a colorless powder began to separate. Enough alcohol was added to bring this material into solution at the boiling point and the solution was set aside to crystallize. The bromo compound separated in a very pure condition in the form of long, slender needles (0.8 g.). The substance distils without decomposition and may be recovered unchanged after prolonged boiling with alcoholic alkali. No coloration is produced with cold concd. sulfuric acid, but on heating the solution acquires an intense red color. The melting point is 179°.

Anal. Calcd. for $C_{20}H_{17}Br$: C, 71.21; H, 5.08. Found: C, 71.22; H, 5.15.

Summary

In extending earlier investigations various new pleiadenediones, pleiadones and dihydropleiadenes have been prepared and characterized.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

RECEIVED AUGUST 10, 1933
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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ROYAL BAKING POWDER CO.]

Preparation of *l*-Tartaric Acid by the Oxidation of *d*-Gulonic Lactone

BY J. K. DALE AND W. F. RICE, JR.

Fischer and Crossley[1] obtained a 5% yield of potassium acid *d*-tartrate by the oxidation of potassium acid *d*-saccharate with alkaline permanganate. In a patented process Odell[2] claimed a substantial yield of *d*-tartaric acid together with *d*-saccharic acid by the oxidation of *d*-glucose with nitric acid in which was dissolved a small amount of sodium vanadate. It seemed probable that the formation of *d*-tartaric acid in the Odell process might be due, at least in part, to a secondary oxidation of the saccharic acid formed in the early stages of the reaction. This view was substantiated by the fact that the authors obtained *d*-tartaric acid in appreciable yields from both *d*-gulonic and *d*-saccharic lactones by their oxidation with nitric acid containing a trace of a vanadate.

Since *d*-gulonic lactone gives *l*-saccharic[3] acid on oxidation with nitric acid alone, it should give *l*-tartaric acid in addition when oxidized with nitric acid containing a trace of the vanadate catalyst. Moreover the process involves no difficulties and, thanks to the researches[4] that have taken xylose out of the category of rare sugars, *d*-gulonic lactone may be readily obtained.

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(1) Fischer and Crossley, *Ber.*, **27**, 394 (1894).

(2) Odell, U. S. Patent 1,425,605.

(3) Fischer, *Ber.*, **23**, 2611 (1890); Fischer and Stahel, *ibid.*, **24**, 534 (1891).

(4) Hudson and Harding, THIS JOURNAL, **40**, 1601–1602 (1918); Monroe, *ibid.*, **41**, 1002–1003 (1919); Schreiber, Geib, Wingfield and Acree, *Ind. Eng. Chem.*, **22**, 497–501 (1930).

Experimental

d-Gulonic lactone was prepared from xylose by the method of LaForge,[5] with about the same results and yield as obtained by him. Fifty grams of this lactone was dissolved in 25 cc. of water and 105 cc. of concentrated nitric acid containing 0.01 g. of sodium metavanadate. The solution was warmed on a water-bath for a few minutes, but removed when a reaction became noticeable. This oxidation is exothermic and became very vigorous within a few minutes, a copious cloud of nitrogen dioxide being evolved. After the reaction had subsided, the solution was evaporated on a boiling bath until judging by the odor all nitrogen dioxide and volatile acids had been expelled. The somewhat sirupy product was chilled in an ice-bath and oxalic acid dihydrate amounting to 13.6 g. (after drying in air) was removed by filtration. The filtrate diluted to about 100 cc. was one-half neutralized with a 60% potassium hydroxide solution. Within a few minutes crystallization of a mixture of potassium acid *l*-saccharate and potassium acid *l*-tartrate commenced and was complete on standing overnight at room temperature. The crystals were filtered off, washed with a little cold water, then with 60% alcohol. After drying the weight was 22.3 g. One gram required 22.7 cc. of *N*/5 alkali for neutralization. A sample neutralized with potassium hydroxide showed $[\alpha]^{20}_{D}$ −12.4 calculated on the neutral potassium tartrate in the polarized solution. These figures showed the composition of the mixed potassium acid salts to be approximately 39% potassium acid *l*-tartrate and 61% potassium acid *l*-saccharate.

A separation of these salts was effected to a large extent by taking advantage of the far greater solubility of the acid saccharate in boiling water; 21.3 g. of the mixed salts was boiled with 66 cc. of water under a reflux condenser for one-half hour. The undissolved fraction was filtered off, washed with a little water and dried. There was obtained 8.6 g. which was now 95% potassium acid *l*-tartrate. This salt was quantitatively converted to *l*-calcium tartrate by neutralizing and adding a slight excess of 25% calcium acetate solution. The small amount of *l*-calcium saccharate formed at the same time remained in solution. The calcium salt was powdered, suspended in water on a boiling water-bath and decomposed with the calculated amount of oxalic acid. After filtering off the precipitated calcium oxalate, the acid filtrate was evaporated to a thin sirup which readily crystallized. The crystals were separated from their mother liquor by filtration with suction and washed with a little ice water. The filtrate was half neutralized with potassium hydroxide yielding a crop of pure potassium acid *l*-tartrate.

The acid crystals dried over sulfuric acid were pure *l*-tartaric acid; 0.5 g. titrated 33.3 cc. of *N*/5 alkali, calcd. 33.33 cc.; 1.0 g. in 25 cc. of solution read −2.27° in a 4-dm. tube, hence $[\alpha]^{20}_{D}$ −14.2.

The potassium acid salt from the mother liquor was pure potassium acid *l*-tartrate; 0.5 g. titrated 13.25 cc. of *N*/5 alkali, calcd. 13.29; 1.0 g. exactly neutralized with potassium hydroxide showed $[\alpha]^{20}_{D}$ −28.0, calculated on the basis of the amount of neutral potassium tartrate in the polarized sample.

Calculating the potassium acid salt to tartaric acid and allowing for samples removed for analysis, the yield of *l*-tartaric acid from 50 g. of *d*-gulonic lactone was 6.8 g.

Summary

A yield of 13.6% of *l*-tartaric acid has been obtained by the oxidation of *d*-gulonic lactone, a substance which itself is readily obtained from xylose.

DECATUR, ILLINOIS

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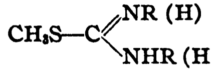
[5] LaForge, *J. Biol. Chem.*, **36**, 347 (1918).

[Contribution from the Department of Chemistry, University of Kansas]

The Synthesis of Heterocyclic Compounds by Means of Isothiourea Ethers

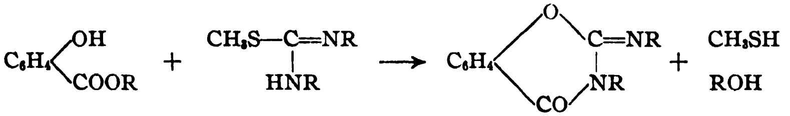
By J. F. Deck and F. B. Dains

While the ureas[1,2,3] and thioureas[4,5] have served in many instances in the synthesis of heterocyclic rings, the use of the thio ethers  $CH_3S—C\begin{cases}NR\ (H)\\NHR\ (H)\end{cases}$ has been very limited. Wheeler and Johnson[6] and their students have employed methyl isothiourea in the synthesis of pyrimidines, and in one instance a substituted quinazoline,[7] but only in this latter case did ring closure involve loss of the $CH_3S—$ grouping.

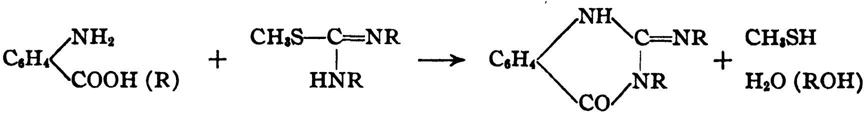
A thiourea of the type $RN{=}C—(SCH_3)NHR$ contains two points of attack; (a) the $SCH_3—$ group can be eliminated as mercaptan on fusion with an amino group or in some cases hydroxyl, (b) the hydrogen of the NHR group can be replaced by an acyl group or the whole grouping split off an amine.

In consequence of this reactivity, a study has been made of the action of these thiourea ethers on *o*-substituted benzenes and on phenylaminoacetic acid, which contain amino, hydroxyl and carboxyl groups. The main types of reactants and the resulting products are briefly outlined as follows

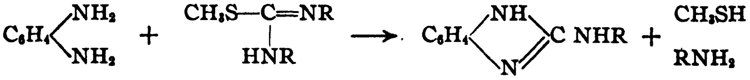
A. Benzoxazines



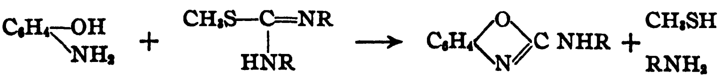
B. Quinazolines



C. Benzimidazoles



D. Benzoxazoles



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(1) Will, *Ber.*, **14**, 1490 (1881).

(2) Will, *ibid.*, **15**, 338 (1882).

(3) Gabriel and Posner, *ibid.*, **28**, 1029 (1895).

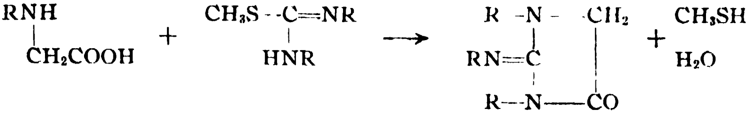
(4) Johnson and Hill, *Am. Chem. J.*, **45**, 356 (1911).

(5) Biltz, *Ann.*, **339**, 265 (1905).

(6) Wheeler and Merriam, *Am. Chem. J.*, **29**, 418 (1903).

(7) Wheeler, Johnson and McFarland, This Journal, **25**, 797 (1903).

E. Imidazolones



$$\begin{matrix}\text{RNH}\\ |\\ \text{CH}_2\text{COOH}\end{matrix} + \begin{matrix}\text{CH}_3\text{S--C=NR}\\ |\\ \text{HNR}\end{matrix} \longrightarrow \begin{matrix}\text{R--N--CH}_2\\ |\quad\ \ |\\ \text{RN=C}\quad |\\ |\quad\ \ |\\ \text{R--N----CO}\end{matrix} + \begin{matrix}\text{CH}_3\text{SH}\\ \text{H}_2\text{O}\end{matrix}$$

Experimental

Preparation of the Methyl Isothiourea Ethers.—Excellent yields (80–90%) of the thio ethers were obtained as follows: thiocarbanilide (450 g.) was dissolved in as little acetone as possible. An equimolecular quantity (250 g.) of dimethyl sulfate was added slowly to the cooled solution with constant shaking. The mixture was then refluxed for three hours and the acetone removed by distillation. The heavy oil was taken up in iced water, filtered and the base precipitated with dilute sodium carbonate. In the case of di-*p*-bromo- (I) and the *m*-nitro-diphenyl thiourea (II), the free base separated and not the salt[8] as with the di-*m*-tolyl- (III), the monobromo-diphenyl- (IV) and α-methyl-β-phenyl thioureas (V).[9]

Synthesis of Benzoxazines.—The fusion of salicylic acid with methyl isodiphenylthiourea or methyl isodi-*o*-tolyl thiourea gave only mercaptans, unchanged acid and diphenyl or di-tolylurea, due evidently to the splitting off of water and its action on the isothioureas at 180°.

$C_6H_4OC(NC_6H_5)NC_6H_5CO$, **2-Phenylimino-3-phenyl-1,3,4-benzoxazine-4-one (VI).**—Methyl salicylate and the diphenyl thio ether were heated at 180° until the evolution of mercaptan ceased. From the melt was isolated a little carbanilide and the benzoxazine. The white needles from chloroform melted at 157–158°. On hydrolysis it gave carbanilide and salicylic acid. Salol[10] which gave a 68% yield of the benzoxazine was used in the later syntheses since the phenol liberated was far less reactive with the thio ether at the temperatures employed, than the methanol. Direct experiment showed that phenol and the methyl ether at temperatures from 180–220° liberated only traces of mercaptan, the reactants being recovered unchanged. The di-*o*-tolyl-benzoxazine was formed when the methyl isothiodi-*o*-tolylurea and phenyl salicylate were heated at 195° for ten hours (VII).

3-*o*-Tolyl-1,3,4-benzoxazine-2,4-dione (VIII) $C_6H_4OCONC_7H_7CO$.—A mixture of the benzoxazine (VII) (2 g.), concentrated hydrochloric acid (1 cc.) and alcohol (50 cc.) was refluxed for four hours. From the neutralized solution after evaporation of the alcohol were isolated *o*-toluidine and the diketo compound.

2-Phenylimino-3-*p*-bromophenyl-1,3,4-benzoxazine-4-one (XI).—This compound resulted when salol was fused with the methyl thio ether of *p*-bromodiphenylurea. The experiment was carried out in order to determine the effect of the substituted bromine on the relative positions of the phenyl and monobromophenyl groups in the benzoxazine ring. The oily product finally crystallized in needles from dilute alcohol (m. p. 135–136°). That the benzoxazine (XI) had the above structure was shown by the fact that on hydrolysis with dilute acid, it gave aniline and 3-*p*-bromophenyl-1,3,4-benzoxazine-2,4-dione (XII) which melted at 214° and contained bromine.

Phenyl Salicylate and the Methyl Thioether of Monophenylurea.—Fusion at 180° or boiling in xylene solution gave the same results. The benzene or xylene solution was extracted with sodium hydroxide (10%). When the alkaline solution was acidified,

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(8) The salt of monophenyl thiourea ether was precipitated as a white crystalline solid in the warm acetone solution, melting at 141–142°. The constitution of this salt was determined as $C_6H_5NHC(SCH_3)NHCH_3HSO_4$ by analysis. N calcd. for $C_8H_{14}N_2O_4S_2$: 10.08; N found, 10.10.

(9) The perchlorate salt melted at 114°.

(10) Titherly, *J. Chem. Soc.*, 97, 208 (1910).

a white solid, soluble also in sodium carbonate, was obtained, which proved to be 2-phenylimino-1,3,4-benzoxazine-4-one, $\overline{C_6H_4OC(NC_6H_5)NHCO}$ (XIII). The crystals from alcohol melted at 189°. When boiled for four hours with sulfuric acid (40%) it gave aniline and the 1,3,4-benzoxazine-2,4-dione (m. p. 224°).[11] This product was identical with the di-one made by heating salicylic acid and urea at 220° for five hours. The original benzene solution after extraction with alkali contained a residue from which nothing definite could be isolated.

Synthesis of Quinazolines.—2-Phenylimino-3-phenyl-4-keto-tetrahydroquinazoline (m. p. 163°) $\overline{C_6H_4NHC(NC_6H_5)NC_6H_5CO}$ (XIV). The reaction product obtained by boiling anthranilic acid and methyl isodiphenylthiourea in xylene or fusion at 170–180° for three hours, was repeatedly extracted with hot dilute hydrochloric acid. The acid solution contained a little aniline and a solid precipitated by alkali which was found to be the above quinazoline. McCoy[12] had previously synthesized this compound by the interaction of benzene, carbodiphenylimide hydrochloride and aluminum chloride. This quinazoline was obtained almost exclusively from methyl anthranilate in boiling nitrobenzene.

3-Phenyl-2,4-diketo-tetrahydroquinazoline (XV).—The residue insoluble in acid from the original fusion mixture was extracted with hot dilute alkali and filtered. Neutralization gave the diketo compound (m. p. 271°) which was evidently formed by the action of water, in fusing at 180°, on the original diphenylquinazoline. Following McCoy's procedure, hydrolysis of the diphenylquinazoline (XIV) with dilute hydrochloric acid at 180° gave aniline and this same diketo derivative,[13,14] thus proving the constitution.

1-Methyl-2,4-diketo-3-phenylquinazoline (XVI).—This product resulted when N-methylanthranilic acid and the methyl thio ether were heated at 185°. Mercaptan was liberated and a little aniline distilled over. The residue contained carbanilide and diketo compound (m. p. 224–225°) due to hydrolysis at the elevated temperature. The compound has been described previously by Fortmann and McCoy[15,16] who obtained melting points of 238 and 223°, respectively.

Tolyl Derivatives.—The fusion of anthranilic acid or its ester or the N-methyl acid with the methyl ethers of di-*o*- and di-*p*-tolylthiourea gave analogous results. Usually a little di-tolylurea was formed (XVII)–(XXI).

2-Phenylimino-4-keto-tetrahydroquinazoline (m. p. 256°).—Anthranilic acid and the methyl ether of monophenylthiourea ether were heated alone and in boiling xylene with the evolution of mercaptan, water and ammonia. The residue was a mixture, partly soluble in acid and in alkali from which no pure compound could be isolated. Wheeler and McFarland[17] had obtained the quinazoline (m. p. 256°) by the fusion of the above reactants, and for the purpose of comparison it was synthesized as follows. Douglass[18] obtained from benzoyl mustard oil and anthranilic acid, the benzoyl thiourea, $C_6H_5CONHCSNHC_6H_4COOH$. Boiling this thiourea with sodium hydroxide (10%) for five minutes closed the ring with loss of benzoic acid. Subsequent methylation gave 2-thio-methyl-4-keto-quinazoline. This heated with aniline at 110° yielded the 2-phenyl-tetrahydroquinazoline (256°) (XXII), which proved to be different from any of the products we had isolated.

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(11) Einhorn and Mettler, *Ber.*, **35**, 3647 (1902).

(12) McCoy, *Am. Chem. J.*, **21**, 131 (1899).

(13) McCoy, *Ber.*, **30**, 1687 (1897); Pawlewski, *ibid.*, **38**, 131 (1905).

(14) Busch, *J. prakt. Chem.*, [2] **51**, 257 (1895); Stewart, *ibid.*, **49**, 318 (1893).

(15) Fortman, *ibid.*, [2] **55**, 130 (1899).

(16) McCoy, *Am. Chem. J.*, **21**, 131 (1899).

(17) Wheeler, McFarland and Johnson, This Journal, **25**, 797 (1903).

(18) Douglass, unpublished thesis, University of Kansas.

Synthesis of Benzimidazoles. 2-Anilino-benzimidazole, $\overline{C_6H_4NHC(NHC_6H_5)N}$ (XXIII).—The reaction between *o*-phenylenediamine and methyl isodiphenylthiourea took place smoothly at 145° with the separation of mercaptan and aniline and was completed after three hours. The product which was weakly basic (the hydrochloride melted at 151–152°) was decolorized with charcoal in an alcohol solution and later recrystallized from benzene (m. p. 188°). It was identical with the imidazolone obtained by Keller[19] from carbodiimide and the diamine. The corresponding tolylamino-benzimidazoles were obtained from the methyl thio ethers of di-*p*- and di-*o*-tolylureas (XXIV)–(XXV).

Synthesis of Benzoxazoles. 1-Anilinobenzoxazoles, $\overline{C_6H_4OC(NHC_6H_5)N}$ (XXVI).—Methyl pseudo diphenylthiourea and *o*-aminophenol were heated at 170° for two hours with the evolution of mercaptan and traces of water and aniline. The reaction product was dissolved in hydrochloric acid (5%) at 65–70° with constant agitation. On cooling a heavy white precipitate settled out. This crystallized from alcohol melted at 170° and proved to be the above benzoxazole which Kalchoff[20] had obtained by fusing 1-mercapto-benzoxazole with aniline. The original hydrochloric acid solution on neutralization gave the same benzoxazole, thus showing that it was a weak base.

The same base (170°) was also formed when the aminophenol was heated with (a) the methyl ether of monophenyl thiourea and (b) the methyl ether of α-methyl-β-phenylthiourea, ammonia and methylamine being eliminated, respectively.

The corresponding tolyl amino benzoxazoles were obtained from the methyl thio ethers of di-*p*- and di-*m*-tolylureas (XXVII)–(XXVIII).

The constitution of these 1-aryl-aminobenzoxazoles was further proved by Kalchoff's synthesis. When 1-mercapto-benzoxazole was heated at 180° with aniline, *p*- and *m*-toluidine, compounds were obtained identical in all respects with the ones described.

Reactions with Substituted Aminophenols.—The methyl ethers were heated with 4-chloro- and 4-nitro-2-aminophenol in order to ascertain whether the presence of chlorine or a nitro group in the ring would affect the reaction in any way. No difficulty occurred and the 4-chloro and 4-nitro-1-aryl aminobenzoxazoles (XXIX)–(XXXIV) were obtained in good yields. It was noted however that the nitroaminophenol reacted more easily than the other aminophenols and its derivatives were best crystallized from glacial acetic acid.

Proof of Structure of the Chloro and Nitro Benzoxazoles: 4-Chloro-mercapto-benzoxazole, $\overline{ClC_6H_3OCSNH}$ (XXXV).—A mixture of the chloraminophenol (50 g.), alcohol (300 cc.) and carbon disulfide (100 g.) was refluxed for thirty-six hours. The mercapto benzoxazole which separated out melted at 261–262°, after recrystallization from glacial acetic acid.

4-Nitro-1-mercaptobenzoxazole $NO_2\overline{C_6H_3OCSNH}$ (XXXVI).—Nitroaminophenol (20 g.), pyridine (5 cc.) and carbon disulfide (50 cc.) were heated for twenty hours at 60°, using a mercury seal. The product was distilled with steam taking care to remove all traces of pyridine, which hindered crystallization. The residue from acetic acid melted at 235–238°, the use of pyridine[21] was necessary since without it no reaction occurred. When the chloro or nitro-mercaptobenzoxazole was heated with the various aryl amines, the same aryl-aminobenzoxazole was obtained as by the previous procedure (XXIX–XXIV). Some difficulty was experienced in purifying the nitro compounds, due possibly to the reducing action of hydrogen sulfide on the nitro group.

Reactions with *o*-Dihydroxybenzene.—Catechol and the methyl thio ether were

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(19) Keller, *Ber.*, **24**, 2498 (1891).

(20) Kalchoff, *ibid.*, **16**, 1825 (1883).

(21) Fry, THIS JOURNAL, **35**, 1545 (1913).

heated for six hours at 180°. Mercaptan was liberated but no ortho condensation product was formed. The only products isolated were diphenylurea and triphenylguanidine which was identified by analysis and comparison with a known specimen. This was the only instance in which this guanidine was found. The results were evidently due to loss of water from the catechol, and its action on the thiourea yielding carbanilide and aniline which in turn with the unchanged methyl ether gave the guanidine.

Synthesis of Imidazolones: $C_6H_5\overline{NC(NC_6H_5)NC_6H_5CH_2CO}$ 1,3-Diphenyl-2-phenylimino-5-imidazolone, (XXXVII).—The ethyl ester of phenylglycine was fused with the methyl thio ether at 180–200° until the evolution of mercaptan ceased, and the melt taken up in benzene. Treatment with alkali removed only traces of acidic material, while extraction with dilute hydrochloric acid dissolved the imidazolone, which was precipitated with alkali. The base after crystallization from dilute alcohol melted at 150–151°. Its constitution was proved by the fact that on hydrolysis with boiling hydrochloric acid (20%), aniline and the well-known diphenylhydantoin (m. p. 138.5°) (XXXVIII) were formed. This same diphenylhydantoin was found in the benzene solution from which the imidazolone (XXXVII) had been removed, a result due to partial hydrolysis in the original fusion.

4-*m*-Nitrobenzal-triphenylimidazolone.—The presence of a reactive methylene group was shown by its condensation with *m*-nitrobenzaldehyde on heating with sodium acetate and acetic acid. The yellow benzal derivative was difficulty soluble and melted at 169–170° (XXXIX).

The following cases (Table XL–XLVII) have shown that this method of synthesis of imidazolones was of general applicability.

Reactions of Phenylaminoethanol.—Molar quantities of the ethanol and the methyl thio ether were heated in boiling xylene. Methyl mercaptan was readily evolved but the reaction products consisted only of diphenyl piperazine and carbanilide. The aminol simply condensed to the piperazine while the water formed reacted with the thiourea. Similar results were obtained with methyl pseudo di-*p*-tolylthiourea.

TABLE I

Text no	Compound	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
I	Methyl isodi-*p*-bromo-diphenylthiourea	$C_{14}H_{12}Br_2N_2S$	129	7.00	6.68
II	Methyl iso-*m*-nitro-diphenylthiourea	$C_{14}H_{13}N_3O_2S$	87–89	14.60	14.80
III	Methyl iso-di-*m*-tolylthiourea	$C_{16}H_{18}N_2S$	97.5	10.37	10.54
IV	Methyl iso-monobromo-diphenylthiourea	$C_{14}H_{13}BrN_2S$	79–80	8.75	8.40
V	Thio-Methyl ether of methyl phenyl urea	$C_9H_{12}N_2S$	58–59	15.55	15.22
	Perchlorate salt of V	$C_9H_{13}B_2S\cdot ClO_4$	114	10.00	9.93
VI	2-Phenylimino-3-phenyl-1,3,4-benzoxazine-4-one	$C_{20}H_{14}N_2O_2$	157–158	8.92	9.05
VII	2-*o*-Tolylimino-3-*o*-tolyl-1,3,4-benzoxazine-4-one	$C_{22}H_{18}N_2O_2$	114	8.18	8.24
VIII	3-*o*-Tolyl-1,3,4-benzoxazine-2,4-dione	$C_{15}H_{11}NO_3$	129–130	5.53	5.62
IX	2-*p*-Tolylimino-3-*p*-tolyl-1,3,4-benzoxazine-4-one[a]	$C_{22}H_{18}N_2O_2$	163–164	8.18	8.01
X	3-*p*-Tolyl-1,3,4-benzoxazine-2,4-dione[b]	$C_{15}H_{11}NO_3$	221	5.53	5.41
XI	2-Phenylimino-3-bromophenyl-1 3,4-benzoxazine-4-one	$C_{20}H_{13}BrN_2O_2$	135–136	7.12	6.64
XII	3-*p*-Bromophenyl-1,3,4-benzoxazine-2,4-dione	$C_{14}H_8BrNO_4$	214	4.40	4.83
XIII	2-Phenyl-1,3,4-benzoxazine-4-one	$C_{14}H_{10}N_2O_2$	189	11.76	11.75
XIV	2-Phenylimino-3-phenyl-4-ketotetrahydroquinazoline	$C_{20}H_{15}N_3O$	163	13.41	13.19
XV	3-Phenyl-2,4-diketo-tetrahydroquinazoline	$C_{20}H_{10}N_2O_2$	271	11.76	11.72
XVI	1-Methyl-3-phenyl-2-keto-tetrahydroquinazoline	$C_{15}H_{12}N_2O_2$	224.5	11.11	10.98
XVII	2-*p*-Tolylimino-3-*p*-tolyl-4-ketotetrahydroquinazoline	$C_{22}H_{19}N_3O$	149	12.32	12.08
XVIII	3-*p*-Tolyl-2,4-diketo-tetrahydroquinazoline[c]	$C_{15}H_{12}N_2O_2$	273	11.11	11.25
XIX	1-Methyl-2-keto-3-*p*-tolyl-4-ketotetrahydroquinazoline	$C_{16}H_{14}N_2O_2$	190	10.52	10.47
XX	2-*o*-Tolylimino-3-*o*-tolyl-4-ketotetrahydroquinazoline	$C_{22}H_{19}N_3O$	157–159	12.32	11.96

TABLE I (*Concluded*)

Text no.	Compound	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
XXI	3-*o*-Tolyl-2,4-diketo-tetrahydroquinazoline[d]	$C_{15}H_{12}N_2O_2$	238–239	11.11	11.32
XXII	2-Phenylimino-4-keto-tetrahydroquinazoline	$C_{14}H_{11}N_3O$	256	17.71	17.80
XXIII	2-Anilinobenzimidazole	$C_{13}H_{11}N_3$	188	20.10	19.97
XXIV	2-*p*-Tolylaminobenzimidazole[e]	$C_{14}H_{13}N_3$	207	18.83	18.62
XXV	2-*o*-Tolylaminobenzimidazole[e]	$C_{14}H_{13}N_3$	182	18.83	18.84
XXVI	1-Anilino-benzoxazole	$C_{13}H_{10}N_2O$	170	13.33	13.01
XXVII	1-*p*-Tolylaminobenzoxazole	$C_{14}H_{12}N_2O$	178	12.50	12.29
XXVIII	1-*m*-Tolylaminobenzoxazole	$C_{14}H_{12}N_2O$	146	12.50	12.50
XXIX	4-Chloro-1-phenylaminobenzoxazole	$C_{13}H_9ClN_2O$	199	11.45	11.21
XXX	4-Chloro-1-*p*-tolylaminobenzoxazole	$C_{14}H_{11}ClN_2O$	204.5	10.81	10.54
XXXI	4-Nitro-1-phenylaminobenzoxazole	$C_{13}H_9N_3O_3$	235	16.47	16.62
XXXII	4-Nitro-1-*p*-tolylaminobenzoxazole	$C_{14}H_{11}N_3O_3$	222–224	15.61	15.65
XXXIII	4-Nitro-1-*o*-tolylaminobenzoxazole	$C_{14}H_{11}N_3O_3$	173–174	15.61	15.23
XXXIV	4-Nitro-1-*m*-tolylaminobenzoxazole	$C_{14}H_{11}N_3O_3$	207	15.61	15.27
XXXV	4-Chloro-1-mercaptobenzoxazole	C_7H_4ClNOS	262	7.56	7.50
XXXVI	4-Nitro-1-mercaptobenzoxazole	$C_7H_4N_2O_2S$	235–238	14.28	14.09
XXXVII	1,3-Diphenyl-3-phenylimino-5-imidazolone	$C_{21}H_{17}N_3O$	150–151	12.81	12.84
XXXVIII	1,3-Diphenyl-2-keto-5-imidazolone	$C_{15}H_{12}N_2O_2$	138.5	11.11	10.99
XXXIX	1,3-Diphenyl-3-phenylimino-4-*m*-nitrobenzal-5-imidazolone	$C_{28}H_{20}N_4O_3$	170	12.10	11.82
XL	1-Phenyl-2-*p*-tolylimino-3-*p*-tolyl-5-imidazolone[f]	$C_{23}H_{21}N_3O$	158	11.84	11.55
XLI	1-*p*-Tolyl-2-keto-3-phenyl-5-imidazolone[g]	$C_{16}H_{14}N_2O_2$	153	10.52	10.34
XLII	*m*-Nitrobenzal derivative of XL	$C_{30}H_{24}N_4O_3$	156	11.48	11.22
XLIII	1-*o*-Tolyl-2-*o*-tolylimino-3-phenyl-5-imidazolone[h]	$C_{23}H_{21}N_3O_4$	130	11.84	11.88
XLIV	1-*o*-Tolyl-2-keto-3-phenyl-5-imidazolone[i]	$C_{16}H_{14}N_2O_2$	126	10.52	10.48
XLV	1-Phenyl-2-phenylimino-3-*p*-tolyl-5-imidazolone[j]	$C_{22}H_{19}N_3O$	126	12.31	12.33
XLVI	1-Phenyl-2-keto-3-*p*-tolyl-5-imidazolone[k]	$C_{16}H_{14}N_2O_2$	155	10.52	10.62
XLVII	1-Phenyl-2-phenylimino-3-*p*-tolyl-4-*m*-nitrobenzal-5-imidazolone	$C_{29}H_{22}N_4O_3$	176	11.81	11.56

[a] From salol and methyl isodi-*p*-tolylthiourea at 180°.

[b] From the hydrolysis of IX with dilute hydrochloric acid.

[c] From the original reaction product and the hydrolysis of XVII.

[d] McCoy, *Am. Chem. J.*, **21**, 131 (1899).

[e] From *o*-phenylenediamine and the methyl thio ethers of *o*- and *p*-di-tolylthiourea, besides toluidine. The hydrochloride of XXIV melted at 174° and of XXV at 89–90°.

[f] From ethyl phenylaminoacetate and methyl isothio-di-*p*-tolylurea.

[g] From the hydrolysis of XL, and the original reaction mixture.

[h] From the glycine and methyl isothio-di-*o*-tolylurea.

[i] From the original reaction mixture and the hydrolysis of XLIII.

[j] From the ethyl ester of *p*-tolylglycine and the methyl thio ether.

[k] From the reaction product in XLV.

Summary

The methyl ethers of the substituted thioureas gave fused heterocyclic rings with *o*-substituted benzenes. The following types were synthesized: benzoxazines from esters of salicylic acid, quinazolines from anthranilic acid, benzimidazoles from *o*-phenylenediamine, benzoxazoles from *o*-aminophenols, imidazolones from aryl glycines. Catechol and phenylaminoethanol gave no fused ring derivatives. The thioureas were easily methylated using methyl sulfate in acetone solution and then neutralizing the salts formed with dilute sodium carbonate.

LAWRENCE, KANSAS

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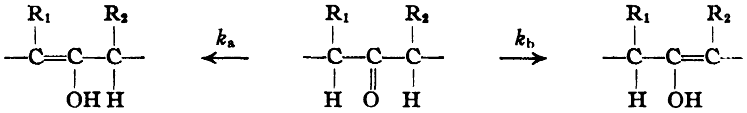
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Enolization as Directed by Acid and Basic Catalysts. I. The Acid-Catalyzed Enolization of Menthone

BY PAUL D. BARTLETT AND JOHN R. VINCENT

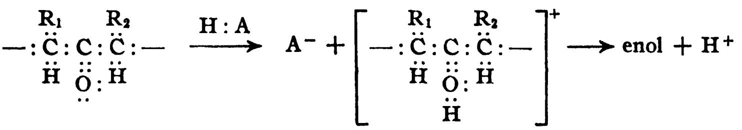
There are two reactions of ketones which have long been considered to involve enolization as a rate-controlling step. These are halogenation in the α-position to the carbonyl group,[1] and racemization (where the center of asymmetry is the α-carbon atom).[2] In a ketone having hydrogen atoms available for enolization on both sides of the carbonyl group, two enols are possible



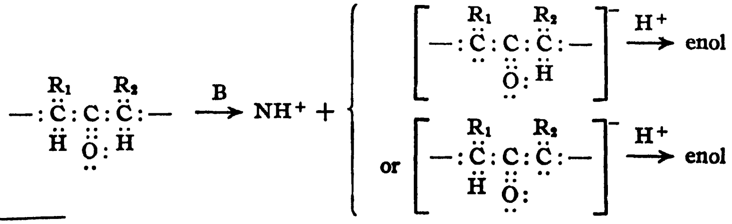
$$\underset{\mathrm{OH}}{\overset{R_1}{-C}}{=}C{-}\underset{\mathrm{H}}{\overset{R_2}{C}}{-} \xleftarrow{k_a} \underset{\mathrm{H}}{\overset{R_1}{-C}}{-}\underset{\mathrm{O}}{C}{-}\underset{\mathrm{H}}{\overset{R_2}{C}}{-} \xrightarrow{k_b} \underset{\mathrm{H}}{\overset{R_1}{-C}}{-}C{=}\underset{\mathrm{OH}}{\overset{R_2}{C}}{-}$$

If the carbon atom bearing R_1 is asymmetric, the rate of racemization measures k_a, while the rate of halogenation of the same ketone measures $(k_a + k_b)$. A kinetic method is thus available for determining the relative amounts of enolic hydrogen furnished by the carbon atoms bearing the radicals R_1 and R_2.

This proportion is of interest in view of modern theories of the mechanism of enolization. The results of Watson and his co-workers[3] on the acid and basic catalysis of bromination of substituted acetones are best interpreted by postulating separate paths for the catalysis by acids and by bases, in accordance with the ideas of Lapworth,[4] Lowry,[5] and others. An acid, HA, functions catalytically by delivering a proton to the position on oxygen which it will occupy in the enol



A base, B, functions catalytically by removing a mobile proton from one of the α-carbon atoms



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[1] For a review of the literature, see Watson, *Chem. Rev.*, **7**, 173 (1930).

[2] Beckmann, *Ann.*, **250**, 360 (1889); up-to-date discussion by Wagner-Jauregg in "Stereochemie," ed. Freudenberg, Franz Deuticke, Vienna, 1933, p. 858.

[3] Hughes, Watson and Yates, *J. Chem. Soc.*, 3318 (1931); Watson and Yates, *ibid.*, 1209 (1932).

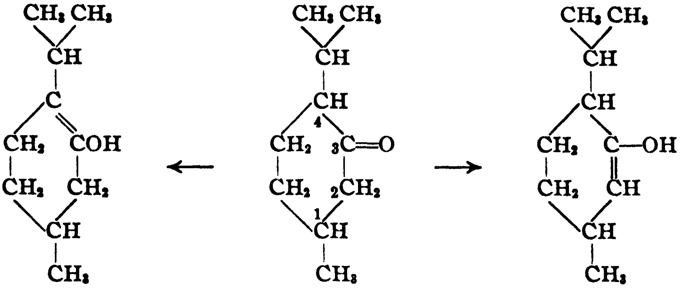
[4] Lapworth and Hann, *ibid.*, **81**, 1513 (1902).

[5] Lowry, *Chem. Rev.*, **4**, 231 (1927).

the point of attack depending upon which substituent, R_1 or R_2, more greatly enhances the removal of the nearby hydrogen as a proton.

The relative amounts of the two enols formed with a given catalyst may be expected to be some function of the polarity of R_1 and R_2, as is the case with the relative susceptibility to acid and basic catalysis of series of esters,[6] and of substituted acetones.[7] We have chosen the readily available *l*-menthone as a first example to which to apply the method. Under typical conditions of acid catalysis, we have found that 79 ± 5% of the enol produced is the form I (Δ^3-menthenol-3)

I



II

Our results using nitric acid as a catalyst in glacial acetic acid at 30.9° are

Average rate of inversion, 0.00872	
Average rate of iodination: using 2 cc. stock iodine solution	0.01109
using 1 cc. stock iodine solution	0.01101
Average	0.01105

0.00872/0.01105 = 78.7% = fraction of enolic hydrogen furnished from C-atom 4.

Method.—The catalytic "inversion" of *l*-menthone has been much studied.[8] The reaction is slow in aqueous media, but proceeds at a measurable rate with strong acids or sodium alkoxides in alcohols. Since it was necessary for us to measure inversion and halogenation in the same medium, we have chosen glacial acetic acid for a solvent, which is inert to halogens in the presence of acids and bases alike.

For the halogenation experiments we used iodine, following the reaction by a colorimetric method. Iodine reacts reversibly with menthenol, according to the equation $C_{10}H_{18}O + I_2 \rightleftharpoons C_{10}H_{17}OI + HI$, and in acid media the equilibrium is largely to the left. Therefore hydrochloric and sulfuric acids, though good enolization catalysts, do not bring about iodination of menthone. Nitric acid in glacial acetic acid, however, oxidizes hydrogen iodide to iodine, thus making the reaction effectively irreversible. By using small enough amounts of iodine relative to the nitric acid present the concentration of the latter can be kept constant during reaction.

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(6) Ingold, *J. Chem. Soc.*, 1033 (1930).

(7) Hughes, Watson and Yates, *ibid.*, 3318 (1931); Watson and Yates, *ibid.*, 1207 (1932).

(8) Beckmann, *Ann.*, **250**, 355 (1889); Tubandt, *ibid.*, **339**, 41 (1904); *ibid.*, **377**, 284 (1910).

The measurement of enolization by the consumption of halogen depends on the latter's reacting instantly with the enol, so that the formation of enol is the rate-controlling step. As is seen by Fig. 1, this is not strictly so in the present case, the reaction of iodine with the enol having a finite rate which slows down the iodine consumption toward the end of a run. A few experiments showed that this is also the case with bromine. This fact makes even the initial rate of reaction to a slight degree a function of the iodine concentration, since it is easily seen that if any enol has time to revert to the keto form before reacting with iodine, the measured rate of enolization will be too low. We have corrected for this effect by applying an equation to the data which yields two constants: the true rate of enolization, and a second constant dependent upon the rate of iodination of the enol. The values for enolization rate obtained from four runs at two different iodine concentrations are in agreement, and we have accepted this value. The information obtained on the rate of iodine addition to the enol is less satisfactory. This reaction may be catalyzed in unknown ways, and even by light.[9] However, its rate is such that it can vary largely without very great effect upon the determined rate of enolization.

Experimental

Preparation of Materials.—*l*-Menthone was prepared by the dichromate oxidation of *l*-menthol:[10] yield, 76%; b. p. 204–207°; $[\alpha]^{30^\circ}_{5461}$ -33.85°.

Nitric acid was purified by distillation from an equal volume of concentrated sulfuric acid in an all-glass apparatus, then drawing dried air through the distillate under 25 mm. pressure until it was colorless. The nitric acid on standing slowly acquired a straw color, which did not affect its catalytic power.

A stock solution of iodine in glacial acetic acid was made up roughly half-saturated, and standardized. It was 0.210 *N*.

Measurement of Inversion.—To make sure that none of the catalysis involved was due to the solvent, a solution of *l*-menthone in glacial acetic acid was kept at room temperature for sixty-five hours. There was no change in optical rotation. 1 cc. of menthone and 1 cc. of nitric acid in 25 cc. of glacial acetic acid solution were used for inversion measurements. The work was carried out in a dark room whose temperature varied less than 0.1° from 30.9° during the experiments. A 1-dm. tube was used for the measurements. The total change of rotation during the reaction was about 2°. In a typical run nine readings were taken, five of them near the beginning and four near the middle of the inversion. The equilibrium value was determined in a solution to which sulfuric acid had been added,

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(9) It may also be that the reaction of hydrogen iodide with nitric acid, and not the addition of iodine to the enol, controls the rate.

(10) "Organic Syntheses," Collective, Vol. I, p. 333.

since this catalyst brought about the inversion very rapidly. Data for an inversion run are

Time interval, minutes	$\text{Log}_{10}(\alpha_1 - \alpha_\infty)/(\alpha_2 - \alpha_\infty)$	$k_1 + k_2$
95	0.3547	0.00860
94	.3501	.00859
93	.3588	.00890
93	.3547	.00879
	Average	.00872
	Mean deviation	1.5%

α_1, α_2 = optical rotations at t_1, t_2, respectively.
α_∞ = optical rotation at equilibrium.
$k_1 + k_2$ = sum of rate constants for both opposing reactions.

Iodination of Menthone.—This was followed colorimetrically, the colorimeter tube being provided with a water-jacket to maintain the temperature at 30.9°. Two pairs of runs were made, both using 1 cc. of nitric acid and 1 cc. of menthone in a total volume of 25 cc. of solution. In one pair 2 cc. of the iodine stock solution was used, in the other pair 1 cc. These concentrations of iodine gave the greatest accuracy of color matching, together with a convenient rate of reaction. Readings could be made within half a minute after mixing the solutions, and the reaction took about ten and five minutes, respectively, in the two series. The original color value was obtained by graphical extrapolation. Sample data are represented in Fig. 1. The constants were determined from the equation

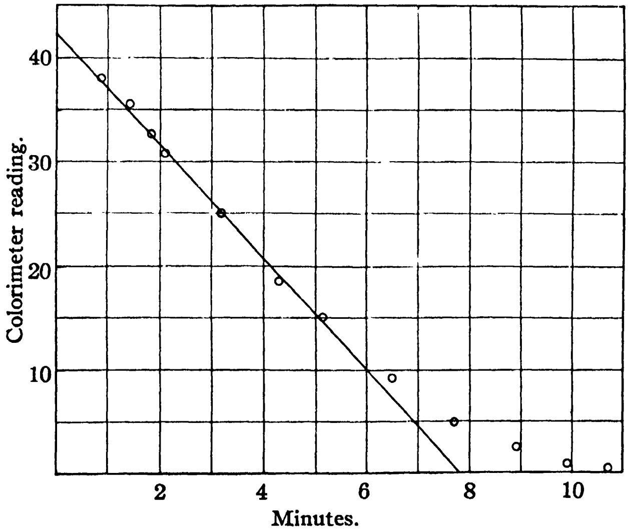

Fig. 1.

$$k_1 = \frac{1}{t}\ln\frac{x_0 + c}{x + c} + \frac{k_4}{ct}\ln\frac{x_0(x + c)}{x(x_0 + c)} \tag{1}$$

by plotting $\frac{1}{t}\ln\frac{x_0 + c}{x + c}$ against $\frac{1}{ct}\ln\frac{x_0(x + c)}{x(x_0 + c)}$, k_1 is the $\left(\frac{1}{t}\ln\frac{x_0 + c}{x + C}\right)$ intercept of the straight line through these points. Figure 2 shows this plot for the data of Fig. 1.

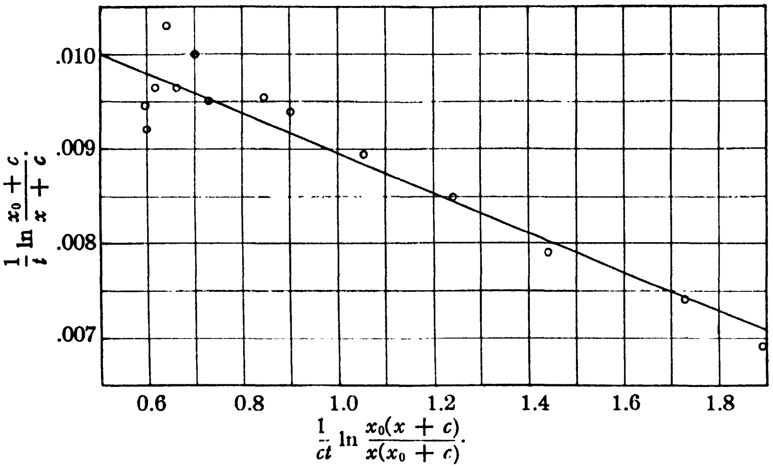

Fig. 2.

Theoretical

Relation between Rate of Enolization and Rate of Inversion.—For a true racemization d-ketone $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ l-ketone, $k_1 = k_2$ and for each two enol molecules formed, one will revert to the d-ketone and one to the l-ketone. Therefore the rate of enolization is equal to $k_1 + k_2$, which is the constant measured in racemization.

The inversion of menthone is not a true racemization, since it is the establishment of an equilibrium between diamers, *l*-menthone and *d*-isomenthone. However, the equilibrium constant between these two forms lies very close to unity,[11] and we have made the assumption that, as in racemization, the rates of enolization of *l*-menthone and *d*-isomenthone are equal. This is supported by some iodination measurements made on "inverted" menthone, in which the rate was the same as that with *l*-menthone, within the experimental error.

Derivation of Equation (1).—Given

$$\text{Menthone} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{menthenol}$$

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[11] Read [*Chem. Rev.*, **7**, 1 (1930)] calculates the equilibrium proportions as 52% *l*-menthone and 48% *d*-isomenthone.

$$\text{Menthenol} + I_2 \xrightarrow{k_3} \text{iodomenthone} + HI$$

$$HI \xrightarrow[\text{instant}]{HNO_3} {}^1/_2\, I_2$$

Let $x = 2[I_2]$

$e = [\text{Menthenol}]$

$x + C - e = [\text{Menthone}]$

C and $[HNO_3]$ are constant then

$$de/dt = k_1(x + c - e) - k_2e - k_3ex$$

Neglecting de/dt in comparison with dx/dt

$$de/dt = 0 = k_1(x + c) - k_1e - k_2e - k_3ex$$

$e = k_1(x + c)/(k_1 + k_2 + k_3x)$

Then $-dx/dt = k_3ex = k_1k_3x(x + c)/(k_1 + k_2 + k_3x)$

Defining $k_4 = (k_1 + k_2)/k_3$, and integrating, we have equation (1)

Discussion

That carbon atom (4) in menthone provides 79% of the enolic hydrogen is in accordance with expectations from the electronic theory. The isopropyl group, like all akyl groups, is an electron-repelling group.[12] The enolization intermediate represented above for acid-catalyzed reaction tends to stabilize itself by drawing an electron pair to the central carbon and saturating the OH group. This electron pair is most readily supplied from that carbon atom which holds electron-repelling substituents.

Summary

1. A quantitative method is described for determining the relative amounts of enolic hydrogen provided from competing positions in an optically active ketone.

2. A probable relationship of this ratio to the chemical character of substituent groups is discussed.

3. The method has been applied to the acid-catalyzed enolization of menthone, and it has been found that 79% of the enolic hydrogen is provided by the carbon atom holding the isopropyl group.

MINNEAPOLIS, MINNESOTA

RECEIVED AUGUST 18, 1933
PUBLISHED DECEMBER 14, 1933

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(12) R. Robinson, "Versuch einer Elektronentheorie organisch-chemischer Reaktionen" [Ahrens Sammlung, N. F. No. 14], Stuttgart, 1932, p. 37.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

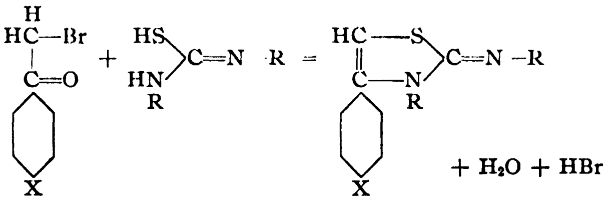
Isomeric 2-Iminotolyl-3-tolyl-4-*p*-chloro and *p*-Bromophenyl-Δ^4-thiazolines

BY RAYMOND M. HANN AND E. EMMET REID

In continuation of a series of researches upon the relation between constitution and color absorption of certain heterocyclic compounds, advantage has been taken of the reactive nature of the ω-halogen acetophenones in condensation reactions with symmetrically disubstituted thioureas to prepare a series of iminoarylthiazolines.

Hantzsch[1] in 1888 published a paper which not only outlined the complete field of the azoles, but was a masterpiece of scientific recapitulation of the particular group in which he was then interested, namely, the thiazoles and their reduction products. This résumé in part reported the pioneer work of Traumann,[2] one of his pupils, who investigated the action of halogen ketones upon thiourea, monoalkyl thioureas and symmetrical dialkyl thioureas. The general utilization of aryl ketones and thioureas was introduced by von Walther,[3] who advanced a theory regarding the mechanism of the condensation reaction involved.

The present paper details the application of the *p*-halogen-phenyl ω-bromomethyl ketones as synthetic agents in the preparation of some isomeric 2-iminotolyl-3-tolyl-4-*p*-halogen-phenyl-Δ^4-thiazolines. The general reaction is



Since the iminothiazolines are strong bases, the halogen acid released during the condensation is reabsorbed to yield the hydrobromide of the base. In the present study no effort was made to isolate the intermediate compounds, but the free base was obtained directly by alkalinization of the reaction mixture. The bases were characterized, however, by preparation of the addition compounds with picric acid.

Experimental

The ω-bromoacetophenone was prepared as described by Rather and Reid[4] and the para halogenated compounds according to the general procedure of Judefind and Reid.[5]

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(1) Hantzsch, *Ann.*, **249**, 1 (1888).

(2) Traumann, *ibid.*, **249**, 31 (1888).

(3) Von Walther, *J. prakt. Chem.*, [2] **75**, 187 (1907).

(4) Rather and Reid, THIS JOURNAL, **41**, 77 (1919).

(5) Judefind and Reid, *ibid.*, **42**, 1044 (1920).

The bromination of *p*-chloroacetophenone was conducted as indicated by Hann, Jamieson and Reid[6] in their study of the phenacyl esters of the fatty acids. The thioureas were obtained by the interaction of mustard oils with the required amine.

The condensation of the *p*-ω-dihalogen ketones with the thioureas was effected by heating molecular proportions of the constituents in absolute alcohol for a period of two hours. In certain cases separation of the thiazoline hydrobromide took place before the expiration of this time period, in which case solution was effected by addition of more alcohol. To the alcoholic solution, which in a majority of cases could be cooled without solid separating, was now added 100 cc. of normal sodium hydroxide and the free thiazoline base precipitated as a gum or crystalline solid. This was washed with water and recrystallized from alcohol or acetone until physical properties were constant. Analyses were conducted by the Kjeldahl–Gunning–Arnold procedure and melting points were obtained with Anschütz thermometers with stems totally immersed. The yields were 80 to 90%. The data are summarized in Table I.

TABLE I

ISOMERIC 2-IMINOTOLYL-3-TOLYL-4-*p*-HALOGEN-PHENYL-$\Delta^{4,5}$-THIAZOLINES

	Compound, phenyl-Δ^4-thiazoline	Appearance	Formula	M. p., °C. (corr.)	Analyses, Kjeldahl-Gunning Arnold Method			
					Weight, g.	Cc. of 1 *N* HCl consumed	Nitrogen, % Found	Calcd.
1	2-Iminophenyl-3-phenyl-4-*p*-chloro-[a]	Colorless micro-crystalline needles	$C_{21}H_{15}N_2SCl$	204	0.1347	7.3	7.59	7.72
2	2-Iminophenyl-3-phenyl-4-*p*-bromo-	Colorless micro-crystalline needles	$C_{21}H_{15}N_2SBr$	206	.1015	5.0	6.90	6.88
3	2-Imino-*o*-tolyl-3-*o*-tolyl-4-*p*-chloro-	Slightly yellow brilliant granules	$C_{23}H_{19}N_2SCl$	132	.1255	6.3	7.03	7.17
4	2-Imino-*o*-tolyl-3-*o*-tolyl-4-*p*-bromo-	Slightly yellow brilliant crystalline aggregates	$C_{23}H_{19}N_2SBr$	123	.1058	4.9	6.49	6.44
5	2-Imino-*p*-tolyl-3-*p*-tolyl-4-*p*-chloro-	Colorless opaque micro-crystalline groups	$C_{23}H_{19}N_2SCl$	227	.1038	5.2	7.02	7.17
6	2-Imino-*p*-tolyl-3-*p*-tolyl-4-*p*-bromo-	Opaque colorless asbestos-like shreds	$C_{23}H_{19}N_2SBr$	239	.1367	6.0	6.15	6.44

[a] The hydrochloride of this base separates in colorless acicular needles melting at 228–229 °C. (corr.)

The basic character of the thiazolines is emphasized by the ease of reaction with picric acid to form beautifully crystalline picrates. One gram of base was dissolved in a minimum amount of alcohol and 10 cc. of alcoholic 10% picric acid added. An immediate separation of the picrate usually occurred and in a number of instances the solution set to a solid mass due to the interwoven structure of the picrate crystals. The picrates were filtered by suction, washed with 95% alcohol and recrystallized from alcohol. Analyses were conducted in this case by the salicyl-sulfonic acid method in order to avoid loss of nitro nitrogen. The description and physical properties of the compounds prepared are included in Table II.

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(6) Hann, Jamieson and Reid, THIS JOURNAL, 52, 818 (1930).

TABLE II

PICRATES OF ISOMERIC 2-IMINOTOLYL-3-TOLYL-4-*p*-HALOGEN-PHENYL-$\Delta^{4,5}$-THIAZOLINES

	Picrates of Δ^4-thiazoline	Appearance
1	2-Iminophenyl-3-phenyl-4-*p*-chlorophenyl-	Golden shimmering platelets
2	2-Iminophenyl-3-phenyl-4-*p*-bromophenyl-	Golden shimmering platelets
3	2-Imino-*o*-tolyl-3-*o*-tolyl-4-*p*-chlorophenyl-	Yellow cleavage-like crystals
4	2-Imino-*o*-tolyl-3-*o*-tolyl-4-*p*-bromophenyl-	Yellow brilliant aggregates
5	2-Imino-*p*-tolyl-3-*p*-tolyl-4-*p*-chlorophenyl-	Yellow brilliant needles
6	2-Imino-*p*-tolyl-3-*p*-tolyl-4-*p*-bromophenyl-	Yellow lustrous granules

			Analyses, salicyl sulfonic acid method			
	Formula	M. p., °C. (corr.)	Weight, g.	Cc. of 1 *N* HCl consumed	Nitrogen, % Found	Nitrogen, % Calcd.
1	$C_{27}H_{18}O_7N_6SCl$	206	0.1331	11.0	11.58	11.84
2	$C_{27}H_{18}O_7N_6SBr$	203	.1209	9.4	10.89	11.01
3	$C_{29}H_{22}O_7N_6SCl$	187	.1237	9.7	10.98	11.30
4	$C_{29}H_{22}O_7N_6SBr$	196	.1145	8.5	10.40	10.54
5	$C_{29}H_{22}O_7N_6SCl$	183	.1115	9.0	11.31	11.30
6	$C_{29}H_{22}O_7N_6SBr$	193	.1713	12.6	10.30	10.54

Summary

p-Chloro and *p*-bromo-ω-acetophenones have been condensed with diphenyl, di-*o*-tolyl and di-*p*-tolyl thioureas to yield 2-imino aryl-3-aryl-4-*p*-halogen-phenyl-Δ^4-thiazolines. The corresponding picrates have also been isolated and described.

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Influence of a Quaternary Ammonium Group on the Hydrogen Atoms of an Adjacent Methylene Group

BY ARNOLD O. JACKSON AND C. S. MARVEL

It is a well-known fact that when two groups, such as carbonyl, cyano, sulfono, nitro and others of this type which are meta-directing in the benzene nucleus, are attached to a methylene group, the methylene group can be alkylated by the action of sodium ethylate and an alkyl halide. The quaternary ammonium salt group $-NR_3^+$ is also a meta-directing group in benzene and it seemed logical to expect that a molecule of the type represented in formula I would be easily alkylated. Such a reaction would be exceedingly useful in the synthesis of complex betaines.

$$[(CH_3)_3NCH_2COOC_2H_5]^+Cl^- \quad \text{I} \qquad [(CH_3)_3NCH_2COOC_2H_5]^+Br^- \quad \text{II}$$

$$[(CH_3)_3NCH_2CONH_2]^+Br^- \quad \text{III} \qquad [(CH_3)_3NCHCNCONH_2]^+Br^- \quad \text{IV}$$

Treatment of carbethoxymethyltrimethylammonium chloride (I) with sodium ethylate and ethyl bromide under the conditions usually used for the alkylation of such molecules as malonic or acetoacetic ester caused only an interchange of halogen with the formation of the bromide (II).

Under the same conditions carbethoxymethyltrimethylammonium bromide (II) could not be alkylated by the action of sodium ethylate and ethyl bromide. The quaternary ammonium salt was recovered unchanged from the reaction mixture. It is thus apparent that one carbonyl and one quaternary ammonium salt group attached to a $-CH_2-$ group will not activate it sufficiently to permit alkylation under the mild conditions used for typical active methylene compounds.

When cyanacetamidotrimethylammonium bromide (IV) was treated with sodium ethylate and an alkyl halide in boiling alcohol, the cyano group was removed and carbamylmethyltrimethylammonium bromide (III) was produced. Sodium ethylate in alcohol produced the same compound from cyanacetamidotrimethylammonium bromide. This removal of the cyano group is analogous to the conversion of tricarbethoxymethane to diethyl ethylmalonate by the action of sodium ethylate and ethyl bromide.[1] It also seems to be related to the cleavage of phenacylpyridinium salts by alkali which has recently been described by Fuson and Babcock.[2] The recovery of carbamylmethyltrimethylammonium bromide (III) in this experiment shows that it does not alkylate in the presence of sodium ethylate and an alkyl halide.

Experimental

Bromocyanacetamide.—To a solution of 21 g. of cyanacetamide in 500 cc. of glacial acetic acid, 40 g. of bromine was added dropwise. The solution was stirred during the bromination. The first half of the bromine was added at room temperature. Then the reaction mixture was placed in a water-bath and warmed slightly so that when all of the bromine had been added the temperature was about 40°. When the color due to bromine had disappeared, the solvent was removed under reduced pressure and the residue was recrystallized from water. The yield was 25 g. (61% of the theoretical amount) of a product of m. p. 176–177°.

Anal. Calcd. for $C_3H_3ON_2Br$: Br, 49.08. Found: Br, 48.86.

TABLE I

TRIMETHYLAMMONIUM HALIDE DERIVATIVES

Compound prepared	Halogen derivative used	Solvent for crystallization	Yield, %	M. p., °C.	Analyses, % Calcd.	Found
$[(CH_3)_3NCH_2COOC_2H_5]Cl$	$ClCH_2COOC_2H_5$	Alcohol and ether	72	166–167[a]	Cl, 19.56	19.31 19.63
$[(CH_3)_3NCH_2COOC_2H_5]Br$	$BrCH_2COOC_2H_5$	....	67	158–159	[b]	
$[(CH_3)_3NCH_2CONH_2]Br$	$BrCH_2CONH_2$	Abs. alcohol	86	203–204	C, 30.46 H, 6.5 N, 14.2 Br, 40.61	30.47 6.50 13.4 40.9
$[(CH_3)_3NCH(CN)-CONH_2]Br$	$BrCH(CN)-CONH_2$	Abs. alcohol	77	199–200	Br, 36.03	36.04

[a] Koeppen, *Ber.*, 38, 167 (1905), reports the product as melting at 143–144°.

[b] Characterized previously by Hunt and Renshaw, *J. Pharmacol.*, 25, 319 (1925).

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(1) Michael, *Am. Chem. J.*, 14, 500 (1892).

(2) Babcock and Fuson, THIS JOURNAL, 55, 2946 (1933).

Quaternary Ammonium Salt.—The quaternary ammonium salts were prepared in the usual fashion from the halogen derivatives and alcoholic trimethylamine solution. The properties are recorded in Table I.

Alkylation Experiments.—To a solution of 0.45 g. of sodium in 75 cc. of absolute alcohol was added 3.6 g. of carbethoxymethyltrimethylammonium chloride in 50 cc. of alcohol and 2.5 cc. of ethyl bromide. The reaction mixture was boiled under a reflux condenser for about ten hours. The reaction mixture was cooled to room temperature and filtered to remove inorganic salts. The solution was concentrated to about 40 cc. under reduced pressure and on cooling a small amount of a compound melting at 294–295° was obtained. This compound (A) was not the desired ethylated derivative and it contained bromine. The analysis did not give a clue to its identity.

Anal. Found: Br, 23.62, 23.53; N, 8.38.

The mother liquors from compound (A) were diluted with dry ether. In this manner a second bromine-containing compound, m. p. 158–160°, was obtained. This material was shown to be carbethoxymethyltrimethylammonium bromide by analysis and by taking a mixed melting point with an authentic specimen of this bromide.

In a similar manner carbethoxymethyltrimethylammonium bromide was treated with sodium ethylate and ethyl bromide. A small amount of the compound melting at 294–295° was obtained but most of the starting material was recovered unchanged.

To a solution of 0.4 g. of sodium in 150 cc. of absolute alcohol was added 4 g. of cyanacetamidotrimethylammonium bromide. This solution was refluxed with ethyl bromide and then worked up as described in the preceding alkylation experiments. The product obtained melted at 204–205° and by analysis and mixed melting point determinations it was identified as carbamylmethyltrimethylammonium bromide. The same product was obtained in 90% yield by treating cyanacetamidotrimethylammonium bromide with alcoholic sodium ethylate.

Summary

Treatment of the compounds $[(CH_3)_3NCH_2COOC_2H_5]^+Cl^-$ and $[(CH_3)_3NCH_2COOC_2H_5]^+Br^-$ with sodium alcoholate and ethyl bromide did not effect alkylation of the —CH_2— group. Cyanacetamidotrimethylammonium bromide was converted to carbamylmethyltrimethylammonium bromide by the action of hot alcoholic sodium ethylate.

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The Replacement of Groups by Hydrogen in Certain Substituted Methanes. α-Tribromoacetophenones

BY C. HAROLD FISHER

It has been long known that methanes highly substituted with certain groups and/or atoms (nitro, acyl, aroyl, halogen, cyano, etc.) undergo replacement of a group or atom by hydrogen, when treated with reagents such as alkali,[1] hydrazine hydrate[2] and sodium iodide;[3] and sufficient data are at hand already to predict in some cases which group will be replaced. For instance, it has been shown that a bromine atom will undergo replacement[4] before a chlorine atom, and that generally an acyl or aroyl group is even more easily replaced.[5] A methane substituted with three bromine atoms and a benzoyl group (tribromoacetophenone) has not been studied from this standpoint, although some work[6] has been done which indicates that a bromine atom instead of the benzoyl group (excepting when alkali is used) is replaced by hydrogen in certain α-tribromoacetophenones. The present paper is a report of work which shows conclusively that in most of the cases studied a bromine atom of tribromomethyl aryl ketones has a predominating tendency to be replaced by hydrogen. A hindered tribromomethyl ketone, α,α,α,3,5-pentabromoacetylmesitylene[7] (I), was selected for this study to eliminate complicating reactions of the carbonyl group, and because of its availability. The products (3,5-dibromo-β-isodurylic acid[8] and tetrabromoacetylmesitylene (IV)[7]) formed by replacement of either the benzoyl group or a bromine atom of this ketone are solids which may be easily identified.

When potassium iodide and α,α,α,3,5-pentabromoacetylmesitylene (I) were allowed to react in acetone at room temperature two bromine atoms were replaced by hydrogen, the product being α,3,5-tribromoacetylmesitylene (II). The structure of this tribromo ketone (II) was established by its reactions and synthesis. Reduction with zinc and acetic acid gave 3,5-dibromoacetylmesitylene (III),[7] and treatment with sodium hypobromite

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(1) Norris and Thorpe, *J. Chem. Soc.*, **119**, 1203 (1921); Macbeth *et al.*, *ibid*, **117**, 880 (1920); **119**, 355 (1921); Baker, *ibid.*, 2419 (1931); Woodward and Fuson, THIS JOURNAL, **55**, 3472 (1933); Neff, *Ann.*, **308**, 329 (1899); Hantzsch and Rinckenberger, *Ber.*, **32**, 628 (1899); see also Cope, THIS JOURNAL, **54**, 1250 (1932); this and other lists of references in this paper are not necessarily complete.

(2) (a) Macbeth and students, *J. Chem. Soc.*, 1870 (1931); 1248 (1926); **121**, 2173 (1922); (b) Howk and McElvain, THIS JOURNAL, **55**, 3372 (1933).

(3) (a) Backes, West and Whiteley, *J. Chem. Soc.*, **119**, 377 (1921); (b) Willstätter and Hottenroth, *Ber.*, **37**, 1775 (1904); (c) Birkenbach, Kellemann and Stein, *ibid.*, **65**, 1071 (1932); (d) Goldschmidt and Nagel, *ibid.*, **63**, 1212 (1930); (e) Löwenbein and Schuster, *Ann.*, **481**, 106 (1930); see Ref. 2b.

(4) Gott and Hunter, *J. Chem. Soc.*, **125**, 442 (1924); Zincke and Gerland, *Ber.*, **21**, 2388 (1888).

(5) (a) Myddleton, Barrett and Seager, THIS JOURNAL, **52**, 4405 (1930); (b) Bull and Fuson, *ibid.*, **55**, 3424 (1933).

(6) Fisher, Snyder and Fuson, *ibid.*, **54**, 3665 (1932).

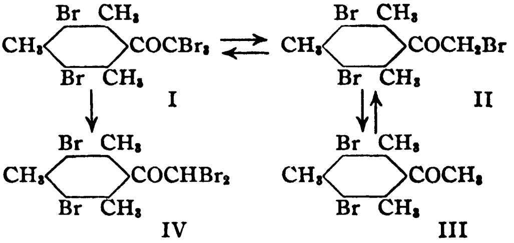
(7) Fisher, *ibid.*, **55**, 4241 (1933).

(8) Shildneck and Adams, *ibid.*, **53**, 351 (1931).

caused the formation of the pentabromo ketone (I). The synthesis of II was carried out by treating an acetic acid solution of 3,5-dibromoacetylmesitylene (III) with one mole of bromine. It seems probable that α,α,3,5-tetrabromoacetylmesitylene (IV) is an intermediate in the reduction of the pentabromo ketone (I) to the tribromo ketone (II), since the action of potassium iodide on the sharply-melting substance[7] composed of equimolar quantities of the penta- and tetra-bromo ketones (I and IV) yielded the same tribromo ketone (II).

Ethylmagnesium bromide in excess reacted with the pentabromo ketone (I) to yield the partially dehalogenated ketone (IV). Presumably, this reaction proceeded according to the equation recently proposed for the dehalogenation of α-halo ketones by Grignard reagents.[9]

The reaction of hydrazine hydrate with pentabromoacetylmesitylene (I) in alcohol proceeded very slowly, and was not complete, as judged by the volume of nitrogen liberated, even after fifty-six hours. The product isolated was tetrabromoacetylmesitylene (IV). The same transformation (I to IV) was brought about also by the action of phenol. The dehalogenation of α-bromo ketones by phenols has been shown to proceed, in the cases[6,10] previously studied, with the formation of *p*-bromophenol. That pentabromoacetylmesitylene (I) reacts more readily with phenol than does the tetrabromo ketone (IV) is shown by the fact that the sharply-melting addition product[7] of these two ketones (I and IV) reacted under the same conditions with phenol to give a good yield of tetrabromoacetylmesitylene (IV).



Conditions (refluxing for one hour) similar to those used for the dehalogenation with acetone of α-bromo-α,α-diphenylacetophenone[3e,11] caused no appreciable reaction in the case of pentabromoacetylmesitylene (I). Dehalogenation to the tetrabromo ketone (IV) proceeded smoothly, however, when the pentabromo ketone (I) was heated for six hours on a steam cone with acetophenone.

It is already well known that α-tribromoacetophenone[5a] and tribromomethyl ketones in general suffer replacement of the benzoyl group (or acyl group) by hydrogen under the influence of alkali. Since this replacement

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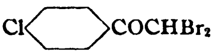
(9) Kohler and Tishler, This Journal, 54, 1594 (1932); see also Ref. 6.

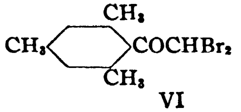
(10) Koelsch, *ibid.*, 53, 1147 (1931).

(11) See also Jackson and Adams, *ibid.*, 37, 3522 (1915).

of the benzoyl group takes place with difficulty and in poor yield when ortho substituents[5b] are present, it seemed possible that dehalogenation might be detected in the case of tribromomethyl aryl ketones thus hindered. The product formed in case of dehalogenation by alkali probably would be the corresponding mandelic acid instead of a dibromomethyl ketone, since alkali converts dibromomethyl aryl ketones[12] into substituted mandelic acids ($RCOCHBr_2 \longrightarrow RCHOHCOOH$). As yet, however, neither the corresponding mandelic acid (indicating dehalogenation) nor the benzoic acid (indicating cleavage) has been isolated after treatment of pentabromoacetylmesitylene (I) with alkali. The starting material was recovered unchanged when cold alkali was used, and the action of hot alkali yielded a mixture from which no pure substance was isolated. Before making a thorough study of the action of alkali on pentabromoacetylmesitylene (I), it seemed advisable to examine the behavior of similarly hindered α-dibromoacetophenones toward alkali.[13] For a preliminary study of this reaction two dibromomethyl ketones were selected which do not have widely different molecular weights and melting points. It was found that under similar conditions α,α-dibromo-4-chloroacetophenone (V,



V



VI

m. p. 94°) dissolves in an aqueous solution of potassium hydroxide several hundred times as rapidly as does α,α-dibromoacetylmesitylene (VI, m. p. 74°).

Experimental

α,3,5-Tribromoacetylmesitylene (II).—Iodine was liberated immediately when 0.278 g. of α,α,α,3,5-pentabromoacetylmesitylene in 10 cc. of acetone was treated with 5.1 cc. of a potassium iodide solution (0.539 g. of potassium iodide in 70 cc. of acetone). After standing for forty-two hours the mixture was filtered to remove a finely divided precipitate, and a dilute solution of sodium thiosulfate was added dropwise to the filtrate until the disappearance of color. The solid which appeared when water was added was crystallized several times from alcohol, coming out as colorless needles melting at 123.5–125° (the amount was insufficient for further purification). When mixed with an authentic sample of α,3,5-tribromoacetylmesitylene (m. p. 126–127°) the m. p. was 125–127°.

The sharply-melting substance[7] (0.278 g.) composed of equimolar quantities of α,α,3,5-tetrabromoacetylmesitylene and α,α,α,3,5-pentabromoacetylmesitylene was treated in the same way with the same quantity of potassium iodide solution used before, and allowed to stand for forty-two hours. The product, isolated and purified as in the above-described experiment, melted at 126–127°. The mixed melting point with α,3,5-tribromoacetylmesitylene was not depressed.

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(12) Engler and Wöhrle, *Ber.*, **20**, 2201 (1887).

(13) The action of alkali on hindered α-dibromoacetophenones is of interest also in connection with the mechanism of the conversion of dibromomethyl aryl ketones into substituted mandelic acids, since retardation of this reaction by steric hindrance might indicate that addition of alkali to the carbonyl group is the first step of the reaction.

α,3,5-Tribromoacetylmesitylene (Second Method).—To 3.2 g. of 3,5-dibromoacetylmesitylene dissolved in 50 cc. of acetic acid was added 24.2 cc. of a bromine solution (16.5 g. of bromine in 250 cc. of acetic acid) during eight minutes, with vigorous stirring. The stirring and heating (water-bath at 55°) were continued twelve minutes. The solvent was then boiled until the solution was concentrated. On cooling 3.3 g. of colorless needles melting at 117–122° appeared. After several crystallizations from alcohol the m. p. was 126–127°.

Anal. Calcd. for $C_{11}H_{11}OBr_3$: C, 33.1; H, 2.8. Found: C, 33.2; H, 2.8.

3,5-Dibromoacetylmesitylene (III).—A mixture of 0.3 g. of α,3,5-tribromoacetylmesitylene, 1.5 g. of zinc dust and 5 cc. of acetic acid was heated under a return condenser on a steam cone for four hours. The reaction mixture was filtered while hot, and after cooling and adding water, washed with ether. The solid which remained after evaporation of the ether was crystallized from alcohol, and found to melt at 146.5–147.5°. It was shown to be 3,5-dibromoacetylmesitylene[7] by the mixed melting point method.

α,α,α,3,5-Pentabromoacetylmesitylene (I).—A solution of 0.2 g. of α,3,5-tribromoacetylmesitylene in 5 cc. of pyridine was added to sodium hypobromite solution (2 cc. of bromine, 6 g. of sodium hydroxide and 55 cc. of water), and the resulting mixture was agitated forty-eight hours. The solid was collected, washed with water and crystallized from alcohol. The melting point, 111.5–113°, was not depressed when mixed with pentabromoacetylmesitylene.[7]

α,α,3,5-Tetrabromoacetylmesitylene (IV). (a) By Action of Grignard Reagent.—An ether solution (5.6 g. of ketone in 75 cc. of ether) of pentabromoacetylmesitylene was added from a dropping funnel with stirring during eight minutes to ethylmagnesium bromide prepared from 1.21 g. of magnesium, 7.4 g. of ethyl bromide and 60 cc. of ether. During the eight-minute period of addition a gray, finely divided precipitate appeared, and the reaction mixture refluxed gently. After being stirred for one-half hour longer the reaction mixture was shaken with dilute hydrochloric acid and ether. Evaporation of the ether layer left needle-like crystals which melted at 142–143.5° after several crystallizations from alcohol.

(b) By Action of Hydrazine.—The reaction was carried out in a modification of the usual Zerewitinoff machine.[14] Pentabromoacetylmesitylene (0.525 g., pulverized) and 10 cc. of alcohol were placed in the reaction flask and treated with 5 cc. of an alcohol solution of hydrazine hydrate (0.0373 g. of hydrazine hydrate per cc. of solution). After 56.5 hours (no increase in quantity of nitrogen occurred during the last thirty hours) the amount of nitrogen liberated was 6.55 cc. (corr.). Based on the equation[2a] which has been written for the hydrazine reaction, the replacement of one atom of bromine should cause the liberation of 10.6 cc. of nitrogen. The product was isolated by adding a large amount of alcohol, and crystallizing from alcohol the precipitate thus formed. The melting point was 142.5–143.5°.

(c) By Action of Phenol.—Pentabromoacetylmesitylene (1.12 g., 0.002 mole) and 0.19 g. (0.002 mole) of phenol were heated on a steam cone for 3.5 hours. After cooling the reaction mixture was triturated with 10% sodium hydroxide solution, filtered and washed with water. Crystallization from alcohol yielded colorless needles melting at 142–143°.

When the same quantities of pentabromo ketone and phenol were heated for two hours on a steam cone the product obtained was the substance[7] (m. p. 108–109°) previously described, composed of penta- and tetra-bromoacetylmesitylene. Phenol (0.19 g.) reacted with 1.12 g. of this substance (m. p. 108–109°), when heated for three and one-half hours on a steam cone, to give tetrabromoacetylmesitylene, m. p. 142–143°.

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[14] The author wishes to acknowledge his indebtedness to Mr. Max Tishler, who supplied this apparatus.

(d) By Action of Acetophenone.—A mixture of 0.56 g. of pentabromoacetylmesitylene and 0.2 g. of acetophenone was heated for six hours on a steam cone. The product solidified on standing several hours; the resulting solid was crystallized several times from alcohol, and was found to be α,α,3,5-tetrabromoacetylmesitylene, melting at 142–143.5°. A lachrymator, probably α-bromoacetophenone, was also formed in the reaction.

The Action of Acetone on Pentabromoacetylmesitylene (I).—The starting material was recovered unchanged after an acetone solution (0.56 g. of ketone in 5 cc. of acetone) of pentabromoacetylmesitylene had been refluxed for one hour. To isolate the product, the reaction mixture was poured into water, and the product which precipitated was crystallized (m. p. 113–114°) from alcohol.

The Action of Alkali on Pentabromoacetylmesitylene (I).—The pentabromo ketone (0.56 g., pulverized) and 50 cc. of a 10% potassium hydroxide solution were shaken for twenty-four hours. The solid was collected by filtration, washed with water and dried. The amount thus obtained was 0.55 g.; the m. p. was 113–114°. A mixed melting point determination indicated that this substance was unchanged starting material.

The action of potassium hydroxide at higher temperatures on 1–5 g. portions of pentabromoacetylmesitylene caused the formation of alkali-soluble products from which no pure substance was obtained.

α,α-Dibromoacetylmesitylene.[6]—A solution of bromine (16 g., 0.1 mole) in acetic acid (20 cc.) was added with mechanical stirring during one-half hour to 8.1 g. (0.05 mole) of acetomesitylene in 40 cc. of acetic acid, which was contained in a three-necked flask equipped with a return condenser, and surrounded by a boiling water-bath. After stirring and heating had been continued for another one-half hour, the reaction mixture was allowed to cool. Scratching caused crystals to appear; the amount of solid was increased by adding water. After several crystallizations from alcohol this solid was obtained as crystals melting at 73–74°; the amount was 6.7 g.

To establish the identity of this product it was converted into α,α,α-tribromoacetylmesitylene by the action of sodium hypobromite according to previously-reported directions.[6] The melting point (68.5–69.5°) of the tribromo ketone thus prepared was not depressed when mixed with α-tribromoacetylmesitylene prepared by the method of Fuson and Walker.[15]

p-Chloromandelic Acid.—After being pulverized in an agate mortar, 2.50 g. (0.008 mole) of α,α-dibromo-4-chloroacetophenone[16] was added to 50 cc. of 10% aqueous potassium hydroxide, and the resulting mixture was mechanically shaken for one-half hour. The undissolved solid was collected, washed with water and dried. This solid (0.1 g. melting at 93.5–94.5°) was starting material.

The filtrate was boiled a few minutes, acidified with hydrochloric acid, and extracted three times with ether. Evaporation of the ether left 1.3 g. of a solid melting at 119–120.5°. After crystallization from ligroin–benzene the m. p. was 119.5–120.5°. The m. p. of p-chloromandelic acid[17] has been given as 120.5–121°.

The Action of Alkali on α,α-Dibromoacetylmesitylene (VI).—The same conditions used in the case of α,α-dibromo-4-chloroacetophenone were employed in this experiment. Pulverized α,α-dibromoacetylmesitylene (2.56 g., 0.008 mole) was agitated with 50 cc. of a 10% potassium hydroxide solution for eighteen hours; 2.25 g. of starting material remained undissolved.

This experiment was repeated, using identical conditions and quantities of reagents. After 194 hours of agitation there remained undissolved 1.80 g. of starting material

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(15) Fuson and Walker, THIS JOURNAL, 52, 3269 (1930).

(16) Fisher, *ibid.*, 55, 4594 (1933).

(17) Jenkins, *ibid.*, 53, 2341 (1931).

(mixed melting point). The filtrate was boiled for a few minutes, acidified with hydrochloric acid (a precipitate appeared) and extracted with ether. Evaporation of the ether left a brown oil which changed into a viscous semi-solid on standing. This substance was not identified.

Summary

The behavior of a tribromomethyl aryl ketone toward potassium iodide, ethylmagnesium bromide, hydrazine hydrate, phenol, acetone, acetophenone and alkali has been studied. All these reagents except alkali cause partial dehalogenation of the tribromomethyl ketone.

A preliminary study of the action of alkali on dibromomethyl aryl ketones is described which indicates that the conversion of these dibromo ketones into substituted mandelic acids may be retarded by steric hindrance.

CAMBRIDGE, MASSACHUSETTS

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Triphenylsilicyl Ethylammine $(C_6H_5)_3Si\cdot C_2H_5NH_2$

BY CHARLES A. KRAUS AND HARRY EATOUGH[1]

I. Introduction

The elements of the fourth group form compounds of the type $(R_3A)_2$ where R is commonly an organic radical or, less frequently, hydrogen. The bond A–A has a varying stability depending on the nature of the central element and of the substituents R. In some instances, the compounds dissociate into the free groups R_3A in solution, while in others the dimers are relatively stable. Stability usually increases with decreasing atomic number. These groups are amphoteric, forming compounds R_3AX with negative elements or groups and salts R_3AM with electropositive elements such as the alkali metals. Various of the free groups and their reduction products have been investigated in this Laboratory, particularly those of tin, germanium, and carbon.[2] The free groups are ordinarily formed by reducing the halogen derivatives with the alkali metals in liquid ammonia and the salts are formed by further reduction of the resulting free groups. In the case of silicon, it has not been possible, heretofore, to obtain either the free groups (or their dimers $(R_3Si)_2$) or the alkali metal salts $MSiR_3$ by reduction of the halogen derivatives R_3SiX in liquid ammonia. The reason for this is that the tertiary organic halogen derivatives are ammonolyzed in liquid ammonia.

(1) Rice Fellow in Chemistry at Brown University.

(2) Kraus and Kawamura, THIS JOURNAL, 45, 2756 (1923); Kraus and Sessions, *ibid.*, 47, 2361 (1925); Kraus and Foster, *ibid.*, 49, 457 (1927). For the conductivity of these compounds see Kraus and Callis, *ibid.*, 45, 2624 (1923); Kraus and Johnson, *ibid.*, 55, 3542 (1933); Kraus and Kahler, *ibid.*, 55, 3537 (1933).

It was thought that triphenylsilicon bromide might be reduced to the free group or to its lithium salt by means of lithium in ethylamine, since ethylamine is a much weaker ammonolyzing agent than is liquid ammonia. It was to be expected that triphenylsilicon bromide would be reduced to hexaphenyldisilane in the first instance. The Si–Si bond, however, is very stable and it was not to be expected that this bond would be broken by metallic lithium.

On carrying out the reduction of triphenylsilicon bromide with lithium in ethylamine, reaction occurred without evolution of gas and a soluble product was formed which indicated that reduction, rather than ammonolysis, had taken place. When a second equivalent of lithium was added, a reddish colored solution was formed, indicating the presence of a lithium salt. On evaporating the solvent, after reducing the bromide with one equivalent of lithium, a solid product remained behind which was separated from the inorganic material by distillation at a temperature of 150° in a high vacuum. A well-crystallized solid was obtained which melted at 45°. Analysis indicated that the compound had the formula $(C_6H_5)_3Si\cdot C_2H_5NH_2$, that is, that the product was a molecular compound of the triphenylsilicyl group with one molecule of ethylamine. The molecular weight of the compound in benzene confirmed the results of analysis. The compound appears to be altogether exceptional since it contains an odd number of electrons. Moreover, the compound does not dissociate at 150° in a high vacuum. Because of the unusual nature of the compound, its reactions were carefully studied. Dissolved in boiling ether, the compound dissociates with the formation of hexaphenyldisilane. Treated with water, ethylamine is formed and the silicon compound is left behind. Treated with lithium in ethylamine, lithium triphenylsilicide is formed, which reacts with various reagents as might be expected.

When lithium triphenylsilicide is treated with trimethyltin chloride in liquid ammonia, a reaction occurs in which the tin and silicon atoms are coupled to yield trimethylstannyltriphenylsilicon. The Sn–Si linkage is broken by means of the alkali metals in liquid ammonia or by means of bromine in ordinary solvents.

II. Triphenylsilicyl Ethylammine

Preparation.—A weighed quantity of triphenylsilicon bromide was introduced into the reaction tube A (Fig. 1) and an equivalent quantity of lithium was introduced into the arm B of the reaction tube, whereupon the tube was sealed at G and H. It was then attached to a system similar to that commonly employed in this Laboratory,[3] and exhausted. Fifty cc. of ethylamine, dried with lithium, was condensed in the reaction tube and lithium was added slowly to the ethylamine solution of triphenylsilicon bromide by tapping the side arm B. The lithium went into solution without the appearance of color and without the formation of a precipitate or the evolution of gas. Toward the end, when the reaction slowed down, the contents of the tube were stirred from time to time by boiling the solution.

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(3) Kraus and Nutting, THIS JOURNAL, 54, 1622 (1932).

On completion of the reaction, the ethylamine was distilled into a collecting ampoule and the reaction tube was evacuated. It was then detached from the system, placed in a horizontal position, with the tube C projecting downward, and exhausted by means of a high vacuum pump. A jacket was placed around the tube A and the temperature was raised to approximately 150°. Under these conditions triphenylsilicyl ethylammine condensed in the neck of the reaction tube just beyond the heated portion and, on gently warming the tube, it melted and ran into the receiving tube C.

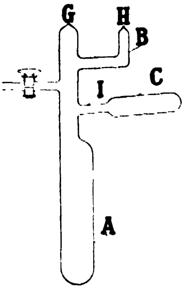

Fig 1.—Reaction tube used in preparation of triphenylsilicylethylammine.

When distillation was completed, the tube was filled with dry nitrogen and the tube C, containing the compound, was sealed off at I. This tube was then introduced into the filling apparatus illustrated in Fig. 2.

A number of weighed, fragile bulbs D with long capillaries were introduced into the expanded tube E (Fig. 2) and the tube C, containing the triphenylsilicyl ethylammine, was introduced into the tube F, the neck of the tube C (previously cut open) projecting downward. The apparatus was exhausted and a bath of hot water was placed around the apparatus to melt the compound, which ran out of its container into the bottom of the expanded tube E. After thoroughly exhausting the apparatus, nitrogen was introduced, which forced the liquid compound through the capillaries into the bulbs. The tube was now allowed to cool and the bulbs were removed, sealed and weighed, along with the capillaries. This gave known samples of the compound for analysis and other purposes.

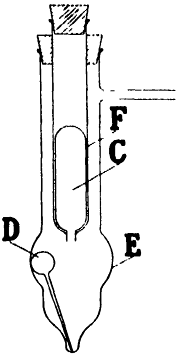

Fig. 2.—Apparatus for preparing weighed samples

Analysis.—It was desirable to analyze for both silicon and nitrogen on the same sample. For this purpose, the sample (in a fragile bulb F) was introduced into a weighed Pyrex tube A (Fig. 3) which, in turn, was introduced into a larger tube B, which was later sealed. The tubes were so fitted that A was held firmly in position. Air-free water was introduced into tube C and the whole apparatus was exhausted. The sample bulb was now broken and the desired quantity of water from C was condensed in A, when the stopcock D was closed. Tubes B and E were then placed in boiling water and heated for four hours in order to complete the dissociation of the compound into ethylamine and hexaphenyldisilane. The aqueous solution of ethylamine was then distilled into the tube E, while the hexaphenyldisilane remained behind in the analysis tube A.

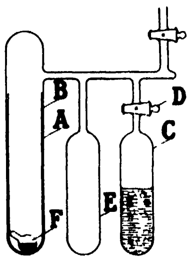

Fig. 3.—Apparatus used in determining ethylamine in triphenylsilicyl ethylammine.

The ethylamine solution was transferred to a beaker and titrated with standard 0.1 *N* hydrochloric acid. After adding a slight excess of acid, the solution was evaporated to dryness and the residue was weighed. This gave the weight of ethylamine hydrochloride. Finally, the hydrochloric acid was redissolved and the chlorine content determined as silver chloride. Tube B was cut open, the analysis tube A was removed and the silicon content of the product was determined by the usual method of oxidation with nitric and sulfuric acids.

Anal. Calcd. for $(C_6H_5)_3Si{\cdot}C_2H_5NH_2$: N, 4.60; Si, 9.22; mol. wt., 304.2. Found: N (by HCl titration), 4.59, 4.57 (by wt. of $C_2H_5NH_3Cl$), 4.58, 4.57 (by wt. of AgCl), 4.67, 4.66; Si, 9.19, 9.17; mol. wt. (cryoscopic in benzene), 292, 287, 290.

Properties.—Triphenylsilicyl ethylammine is a white, crystalline solid which melts at 45°. It is soluble in all of the ordinary organic solvents with the exception of low boiling petroleum ether and alcohol.

Dissociation of Triphenylsilicyl Ethylammine in Ether.—A solution containing 1.23 g. of triphenylsilicyl ethylammine in 25 cc. of dry ether was distilled to remove the solvent and the residue was evaporated to dryness. The residue was taken up in 25 cc. of dry ether and the solution was filtered. There was obtained 0.29 g. of insoluble material which melted at 351–353° and was thus identified as hexaphenyldisilane. The ether solution was boiled under a reflux condenser for half an hour, after which the solvent was again separated by filtration. In this case, there was obtained 0.71 g. of hexaphenyldisilane, thus, making a total of 1.00 g. as against 1.04 g. calculated. This shows that in solvents at higher temperatures the compound is dissociated with the formation of hexaphenyldisilane.

The ethylamine is not replaced by ammonia at liquid ammonia temperatures. Triphenylsilicyl ethylammine does not react with sodium in liquid ammonia to an appreciable extent. It reacts readily with lithium in ethylamine to form lithium triphenylsilicide.

III. Lithium Triphenylsilicide

Preparation.—Lithium triphenylsilicide is readily formed by the direct action of metallic lithium upon triphenylsilicyl ethylammine in ethylamine solution, reaction taking place as follows

$$(C_6H_5)_3Si{\cdot}C_2H_5NH_2 + Li = (C_6H_5)_3SiLi + C_2H_5NH_2$$

It is readily soluble in ethylamine but only slightly soluble in liquid ammonia. Its solubility in liquid ammonia is greatly increased by the presence of small quantities of ethylamine.

The preparation of lithium triphenylsilicide was carried out in a reaction tube of the type usually employed for such purposes in this Laboratory, except that the reaction tube was not provided with the usual central stirring tube. Triphenylsilicyl ethylammine was introduced in a fragile bulb and lithium, cut in small pieces, was introduced into an addition tube from which it could be added to the solution as desired. After evacuating the reaction tube, the fragile bulb was broken and 30 cc. of ethylamine was condensed. The lithium reacted readily with the formation of a reddish colored solution. When all the lithium had been added, the color was so dense that the solution was opaque. On distilling the ethylamine, a white, crystalline solid remained behind.

Reactions of Lithium Triphenylsilicide.—Since the salt cannot be analyzed directly, its constitution was established indirectly by means of certain typical reactions.

(1) **Reaction with Ammonium Bromide.**—If lithium triphenylsilicide is present, it should react with ammonium bromide to form triphenylsilicane according to the equation: $(C_6H_5)_3SiLi + NH_4Br = (C_6H_5)_3SiH + LiBr + NH_3$.

Lithium triphenylsilicide was prepared in ethylamine solution as described above and, after evaporating the ethylamine, 25 cc. of ammonia was condensed in the tube. The salt was only slightly soluble, yielding an orange colored solution. On adding ammonium bromide, the color of the solution diminished in intensity while the excess salt went into solution. After evaporating the ammonia, the inorganic material was extracted with water. The organic residue was dried and dissolved in 95% alcohol, from which triphenylsilane crystallized on evaporation of the solvent under reduced pressure. With the small amount of material available, it was difficult to obtain a high degree of purity. Nevertheless, the product melted at 30–33° as against 36–37° for pure triphenylsilane.

(2) **Reaction with Phenyl Bromide.**—We should expect that lithium triphenylsilicide would react with phenyl bromide to form tetraphenylsilicon according to the equation $(C_6H_5)_3SiLi + C_6H_5Br = (C_6H_5)_4Si + LiBr$.

Lithium triphenylsilicide was prepared as described above; the bulk of the ethylamine was evaporated and ammonia was condensed on the residue. Phenyl bromide was added to the ammonia solution. Reaction took place at once, with disappearance of the orange color due to the lithium salt, and a white precipitate was formed. After evaporating the ammonia, any excess phenyl bromide was extracted with dry ether in which tetraphenylsilicon is insoluble. The tetraphenylsilicon was then extracted with hot benzene. A practically quantitative yield of this compound was obtained which, after crystallization, melted at 230–231°. Polis gives the melting point as 233°.[4]

The above reactions clearly demonstrate the existence of lithium triphenylsilicide. The reactions of this salt are similar to those of corresponding salts of tin, germanium and carbon.

IV. Trimethylstannyltriphenylsilicon

It was to be expected that lithium triphenylsilicide would react with amminotrimethyltin chloride according to the equation

$$(C_6H_5)_3SiLi + (CH_3)_3SnCl{\cdot}NH_3 = (C_6H_5)_3SiSn(CH_3)_3 + LiCl + NH_3$$

Kraus and Foster[5] have prepared a similar compound of germanium and tin which is a white, crystalline solid melting at 88°. The expected silicon compound was obtained as a viscous liquid which could not be crystallized.

Preparation.—Lithium triphenylsilicide was treated with amminotrimethyltin chloride in liquid ammonia. As the chloride was added, the color of the lithium salt disappeared and an oily appearing substance was precipitated. The material in the reaction tube was extracted with petroleum ether (35–55°), the solvent was evaporated on a water-bath and the last traces were removed by means of a vacuum pump. The product was an oily liquid which could not be crystallized even at liquid ammonia temperatures.

The compound was analyzed for combined tin and silicon by oxidation in the usual way. After weighing the combined oxides, the tin oxide was dissolved in concentrated hydrochloric acid and the tin was precipitated as metastannic acid, which was then ignited and weighed as stannic oxide. The weight of the silicon dioxide was determined by difference.

Anal. Calcd. for $(C_6H_5)_3SiSn(CH_3)_3$: Sn, 28.06; Si, 6.63. Found: Sn, 27.65, 27.77; Si, 6.84, 6.69.

Molecular Weight.—The molecular weight of the compound was determined in benzene solution. In all cases the molecular weight was about 50% too high. A series of values was obtained ranging from 599 to 616, while the calculated molecular weight is 423.1. There is no obvious explanation for the discrepancy.

Reactions.—In view of the somewhat unsatisfactory value obtained for the molecular weight, it seemed worth while to characterize the compound somewhat further by its reactions. Accordingly, the following reactions were carried out: (1) reduction by means of sodium in liquid ammonia and subsequent treatment of the products of reduction with methyl iodide; (2) bromination of the compound in ether, separation of the products, and subsequent characterization of the same.

(1).—On treating the compound with sodium in liquid ammonia, one should expect the reaction

$$(C_6H_5)_3SiSn(CH_3)_3 + 2Na = (C_6H_5)_3SiNa + (CH_3)_3SnNa \qquad (1)$$

Reaction proceeded somewhat slowly with the formation of a solution having a yellow color, which is characteristic of the sodium salts of the tertiary alkyl- and aryl-tin or germanium groups. On adding methyl iodide, the color was discharged and a precipitate was formed. If reaction proceeds according to equation (1), it would be expected that the following reactions would take place on adding methyl iodide.

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[4] Polis, *Ber.*, 18, 1541 (1885).

[5] Kraus and Foster, THIS JOURNAL, 49, 457 (1927).

$$(C_6H_5)_3SiNa + CH_3I = (C_6H_5)_3SiCH_3 + NaI \qquad (2a)$$

$$(CH_3)_3SnNa + CH_3I = (CH_3)_4Sn + NaI \qquad (2b)$$

On completion of the reaction, about 15 cc. of 95% ethyl alcohol was added to the solution and then water in sufficient quantity so that, when the solution finally warmed to room temperature, its vapor pressure was less than one atmosphere. This procedure was necessary since, if the ammonia had been evaporated directly from the solution, the tetramethyltin formed in reaction (2b) would have been carried away with the vapor. The solution was transferred to a separatory funnel and extracted with ether. After separation, the ether was dried with anhydrous sodium sulfate and distilled. The residue was taken up in fresh ether and precipitated with alcohol. The precipitate was identified as methyltriphenylsilicon by its melting point 67°. The ether distillate, containing tetramethyltin, was treated with a small quantity of bromine, the ether was distilled and the residue dissolved in petroleum ether. On passing ammonia into the petroleum ether solution, a precipitate was formed. This procedure served to characterize the tetramethyltin since it is known that trimethyltin bromide forms an insoluble precipitate with ammonia.[6]

(2).—On treating the compound with bromine, one should expect the Si–Sn bond to be broken with the formation of an equimolar mixture of triphenylsilicon bromide and trimethyltin bromide. The compound was treated with an equivalent quantity of bromine in ether solution in an apparatus so arranged that, after taking off the ether, the trimethyltin bromide could be separated from the triphenylsilicon bromide by distillation *in vacuo*. After separating the two materials, the apparatus was opened and the two products were extracted with ether and weighed. The results were: wt. sample, 0.4036 g.; $(C_6H_5)_3SiBr$ found, 0.3347 g.; calcd., 0.3236; $(CH_3)_3SnBr$ found, 0.2281; calcd., 0.2326.

The trimethyltin bromide was analyzed for bromine by the usual silver bromide method.

Anal. Calcd. for $(CH_3)_3SnBr$: Br, 30.65. Found: Br, 30.55, 30.54.

The triphenylsilicon bromide was hydrolyzed by means of water and the insoluble silicol was weighed. There were obtained 0.2625 g. as against 0.2636 g. required on the basis of the original weight of material. The bromine was determined as silver bromide as follows: $(C_6H_5)_3SiBr$ (calcd.), 0.3236, AgBr, 0.1784; Br found, 23.46. Calcd. for $(C_6H_5)_3SnBr$: Br, 23.57.

The various reactions supply conclusive evidence that the product obtained by the interaction of trimethyltin bromide with sodium triphenylsilicide in liquid ammonia is simply a combination of the triphenylsilicyl and the trimethylstannyl groups.

In conclusion, all the evidence supports the view that the compound obtained upon treating triphenylsilicon bromide with lithium in ethylamine is a combination of the triphenylsilicyl group with one molecule of ethylamine. We have found no evidence of the formation of a similar compound in the case of tin. Some preliminary investigations on the reduction of triphenylsilicon bromide in methylamine indicate the formation of triphenylsilicyl methylammine,[7] which is distinctly more volatile than the corresponding ethylamine derivative.

V. Summary

Triphenylsilicon bromide and metallic lithium react in ethylamine solution according to the equation: $(C_6H_5)_3SiBr + Li + C_2H_5NH_2 =$

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(6) Kraus and Greer, THIS JOURNAL, 45, 3078 (1923).

(7) F. C. Schmidt, unpublished observations in this Laboratory.

$(C_6H_5)_3Si{\cdot}C_2H_5NH_2 + LiBr$. Triphenylsilicyl ethylammine is a stable compound, melting at 45°, which may be distilled in a high vacuum at 150° without decomposition. In solution in ether and other solvents it decomposes at higher temperatures with the formation of hexaethyldisilane and ethylamine.

It reacts with lithium in ethylamine to form lithium triphenylsilicide. The latter compound reacts with ammonium bromide to form triphenylsilane and with phenyl bromide to form tetraphenylsilicon.

On treating lithium triphenylsilicide with trimethyltin chloride in liquid ammonia solution, the triphenylsilicyl and the trimethylstannyl groups are coupled. This compound is a heavy oil which is stable under ordinary conditions. It reacts with sodium in liquid ammonia to give the sodium salts of the two groups. It reacts with bromine, yielding triphenylsilicon bromide and trimethyltin bromide.

Triphenylsilicyl ethylammine is an exceptional compound in that it has an odd number of electrons and yet is remarkably stable. All the reactions of this compound, however, tend to confirm its constitution as a simple combination of the triphenylsilicyl group with a molecule of ethylamine.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Reactions of Sodium Triphenylstannide with Polyhalogenated Methanes

BY CHARLES A. KRAUS AND HARRY EATOUGH[1]

Compounds such as sodium triphenylstannide react quite generally with the alkyl and aryl halides with the formation of the corresponding sodium halide and the coupling of the alkyl or aryl group with the tin of the triphenylstannyl group. However, in the case of halogen derivatives containing more than one halogen, the reactions usually become more complex and a simple substitution of triphenylstannyl or a similar group for the halogen does not ordinarily occur.

Kraus and Nutting[2] have shown that sodium triphenylgermanide reacts with methylene chloride in part with the formation of di-triphenylgermanylmethane and in part with the formation of monotriphenylgermanylmethane. They account for the formation of the latter compound by a reaction in which a valence of the carbon atom is hydrogenated and triphenylgermanylamine is formed. In the case of chloroform, Kraus and Nutting could find no indication of the formation of the tertiary germanyl derivative, although considerable quantities of the di- and mono-germanyl derivatives were obtained. Kraus and Neal[3] have studied the reaction of sodium trimethylstannide with methylene chloride and with chloroform. With methylene chloride, the stannyl groups are substituted for the halogens, but with chloroform a more complicated reaction occurs in which trimethyltin is formed and an unsaturated methylenic carbon linkage results. With carbon tetrachloride, all the tin was recovered as trimethyltin and the halogen as sodium chloride, but what happened to the carbon was not determined. Similarly, in treating carbon tetrachloride with sodium triphenylgermanide, Kraus and Nutting failed to find what happened to the carbon atom.

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[1] Rice Fellow in Chemistry at Brown University.

[2] Kraus and Nutting, THIS JOURNAL, 54, 1622 (1932).

It seemed of interest to study the reaction of sodium triphenylstannide with the same series of halogenated methanes. In the case of both methylene chloride and chloroform, triphenylstannyl groups were substituted for the halogens, di-triphenylstannylmethane and tri-triphenylstannylmethane being obtained as products of reaction. In the case of carbon tetrachloride, however, practically all the tin was recovered as triphenyltin and the halogen as sodium chloride. No gases were evolved and it was not obvious what became of the carbon atom in this reaction.

It is evident that reactions of compounds of the type MAR_3 with the poly-halogenated methanes are greatly influenced by the nature of the substituent groups R.

Experimental

The experimental procedure was much the same as that already described by Kraus and Nutting in connection with their investigation of the reactions of sodium triphenylgermanide. Triphenyltin was treated with sodium in liquid ammonia in equivalent amount and the organic halide was added to the solution. Reaction took place readily and the resulting products were separated from the residue after the evaporation of ammonia by means of suitable solvents.

Di-triphenylstannylmethane.—The product of reaction of sodium triphenylstannide with methylene chloride was extracted with benzene and the residue obtained on distillation of the solvent and removal of the last traces of benzene by means of a pump was recrystallized from hot petroleum ether. The final product melted at 104.5° (corr.).

The tin content of the compound was determined as stannic oxide in the usual way by oxidation with fuming sulfuric and nitric acids in a weighed Pyrex test-tube.

Anal. Calcd. for $[(C_6H_5)_3Sn]_2CH_2$: Sn, 34.73; mol. wt., 713.8. Found: Sn, 34.63, 34.67; mol. wt., 743, 732.

The molecular weight of the compound was determined cryoscopically in benzene.

Di-triphenylstannylmethane is a white, crystalline solid which melts at 104.5°. It is very soluble in benzene, ether, chloroform and trichloroethylene. It is soluble in hot petroleum ether but only slightly soluble in the cold ether. It is best recrystallized from petroleum ether solution, evaporating slowly at 50°.

Tri-triphenylstannylmethane.—Sodium triphenylstannide was treated with an equivalent quantity of chloroform and, on completion of the reaction and evaporation of the solvent, the residue was extracted with benzene. The benzene extract was distilled, the last traces of solvent were evaporated on a steam-bath, and the product was recrystallized from petroleum ether. The final product melted at 128° (corr.). A very small quantity of triphenyltin was recovered in this reaction and identified by its melting point, 231°. The tin content of the compound was determined as SnO_2 in the usual way.

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[3] Kraus and Neal, THIS JOURNAL, 52, 4426 (1930).

Anal. Calcd. for $[(C_6H_5)_3Sn]_3CH$: Sn, 33.51. Found: Sn, 33.47, 33.49, 33.46.

The molecular weight of the compound was determined cryoscopically in benzene. Calcd. for $[(C_6H_5)_3Sn]_3CH$: mol. wt., 1063. Found: mol. wt., 1040, 1070, 1040.

Tri-triphenylstannylmethane is a white, crystalline solid melting at 128°. It is very soluble in benzene, ether, chloroform and trichloroethylene. It is soluble in hot petroleum ether but only slightly soluble in the cold ether. It is sparingly soluble in alcohol and insoluble in water and liquid ammonia. It is best recrystallized from petroleum ether, evaporating under reduced pressure.

Reaction with Carbon Tetrachloride.—Carbon tetrachloride was found to react readily with sodium triphenylstannide in liquid ammonia. The residue remaining in the reaction tube, after evaporation of ammonia, was extracted with benzene and from this was obtained triphenyltin and a very small amount of material that failed to melt at 360° and which carbonized on heating in a flame. The main product of the reaction was triphenyltin which was identified by its melting point and by analysis. In two reactions there were obtained 0.5794 and 0.5818 g. of sodium chloride, respectively, as against 0.5846 g. required according to the amount of material used. No gases were given off in the course of the reaction and no product could be found indicating what became of the carbon atom of the carbon tetrachloride.

Summary

Di-triphenylstannylmethane and tri-triphenylstannylmethane have been prepared by the action of sodium triphenylstannide on methylene chloride and chloroform, respectively, in liquid ammonia. The corresponding quaternary derivative was not obtained with carbon tetrachloride.

PROVIDENCE, RHODE ISLAND

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The Pyrolysis of *n*-Butane at Low Decomposition Temperatures

BY CHARLES D. HURD, C. I. PARRISH AND F. D. PILGRIM

In the preceding paper[1] it was mentioned that Norris and co-workers studied the pyrolysis of paraffin hydrocarbons at incipient decomposition temperatures and stated that under these conditions the breakdown of the molecule occurred at a specific C–C location. This is in contrast to the results of earlier investigators who, however, employed higher temperatures. In these higher temperature studies, the results pointed to scission at several places in the molecule rather than at an exclusive location although differences in the strengths of the various C–C bonds were evident. It became a matter of importance, therefore, to check Norris' results for they seemed to indicate that this slight difference in the strength of C–C bonds could be capitalized if low enough decomposition temperatures were used.

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[1] Hurd and Pilgrim, THIS JOURNAL, 55, 4902 (1933).

Norris listed 400° as the decomposition temperature of *n*-butane. His work included other hydrocarbons than butane but the conclusions were identical for all. With a contact time of one hour, each was stated to have a definite decomposition temperature which was considered to represent the breaking of an individual C–C bond in the hydrocarbon chain. This conclusion was based on two factors.

First, the presence of a so-called "second break" which was at 450° for *n*-butane and which was usually 30–50° above the "initial decomposition temperature." These "breaks" were made visible by graphical methods. In the graph[2] (for *n*-pentane), rates of decomposition were plotted against °*T*. The points were connected by three straight lines which intersected each other at the "breaks." A smooth curve could have been drawn through the points. It may be noted that a straight line curve with no breaks is obtained by plotting the rates logarithmically (thus, log (rates) *vs.* °*T* or $1/T$).

Second, analyses of the products. In the first temperature range, for example, *n*-butane was stated to give methane and propylene but no ethane or ethylene until the "second break" was reached. It is apparent that the first of these factors is meaningless unless supported by the second. In other words, the crux of the problem is the analysis of the reaction mixture. Inasmuch as the total extent of decomposition is slight the analytical procedure must be capable of detecting traces.

In the present work, pure *n*-butane was passed slowly through an empty Pyrex tube at temperatures which were considerably below Norris' second temperature range. As a matter of fact, we were able to decompose butane at temperatures below its "decomposition point." Norris used a similar method. He passed the gas slowly through a tube (one to two minutes contact time) at a temperature near but below the second break.

In our analysis of the reaction products, the following procedure was employed. The gaseous products were liquefied and separated by precise fractional distillation[3] through a Podbielniak column into four fractions which contained in turn essentially the C_1, C_2, C_3 and C_4 hydrocarbons. Then each fraction was analyzed by the usual absorption and combustion methods.[4]

Our results were not in agreement with those claimed by Norris and coworkers. The products from *n*-butane were found to contain not only methane and propylene but also ethane, ethylene and even small amounts of hydrogen. The same products were observed in the experiments at higher temperatures. Further evidence against Norris' claim is to be found in the recent work of Frey and Hepp,[5] who studied the low temperature (396–398°) pyrolysis of *n*- and isopentane. Since the first temperature range for the former is listed by Norris and Thomson as 391–426° and for the latter as 383–423°, it is evident that Frey and Hepp's temperatures were well within these ranges. Frey and Hepp found that *n*-pentane gave rise to considerable $C_1 + C_4$ hydrocarbons as well as to the more abundant $C_2 + C_3$ hydrocarbons which Norris claimed were the exclusive products. Some hydrogen was found as well. With isopentane, Frey and Hepp found $C_2 + C_3$ hydrocarbons as well as the $C_1 + C_4$ hydrocarbons which were stated by Norris to be formed exclusively.

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[2] Norris and Thomson, THIS JOURNAL, **53**, 3108 (1931).

[3] Podbielniak, *Oil Gas J.*, **28**, 58 (1929); **29**, 235 (1930).

[4] Hurd and Spence, THIS JOURNAL, **51**, 3353 (1929).

[5] Frey and Hepp, *Ind. Eng. Chem.*, **25**, 447 (1933).

These studies with *n*-butane, *n*-pentane and isopentane at low decomposition temperatures suggest that other paraffin hydrocarbons will be found to behave similarly. In other words, there is no evidence of a "first decomposition range," wherein an exclusive C–C bond of a paraffin hydrocarbon may be severed.

Experimental Part

Butane Used.—Two specimens of pure *n*-butane were employed. One was the purified sample from a petroleum fraction, mentioned in the previous paper. It was used in the 400 and 415° experiments. The other was synthetic material and it was used in the 365° experiment.

The synthetic butane was prepared by the hydrolysis of *n*-butylmagnesium bromide. To prepare the latter, pure *n*-butyl bromide, b. p. 100–100.5°, was mixed with four volumes of isoamyl ether[6] (b. p. 170–172°). Magnesium turnings were added and the mixture heated at 100° for half an hour. The Grignard reagent was decomposed (four hours) with dilute sulfuric acid. The effluent butane was scrubbed with concd. sulfuric acid, liquefied and distilled twice through a Davis column; b. p. 0.0–0.5°. It did not decolorize bromine in carbon tetrachloride. Three runs (one mole quantities in each) gave yields of 55–70%.

Pyrolysis.—Experiments, using the same set-up as described in the previous paper, were carried out at 415, 400 and 365°. All temperatures were ±5°. Immediately prior to the 365°-experiment, the temperature recorder (chromel–alumel thermocouple) was calibrated and found to be correct at the boiling point of mercury: found, b. p. of mercury 355–356° at 744.6 mm. This coincides with the accepted value.

Experiment at 415°.—The details follow: butane used, 15.47 liters; rate of flow, 106 cc./min. Exit gas: volume, 16.78 liters; rate of flow, 115 cc./min. Room temp., 29°. Volume of heated part of tube, 460 cc. Contact time, 1.8 minutes. Extent of decomposition, 5%.

Analysis.—The exit gas was collected and subjected to fractional distillation on the Podbielniak column. Liquid air was used as the cooling agent. Four fractions were collected (see Table I) each fraction showing distinct temperature plateaus when the temperature was plotted against the gaseous volume of the distillate. Each fraction was analyzed separately in the usual way (absorption and combustion methods). Acetylenes were not formed. Whether any butene was formed cannot be answered. No more than 13 cc. ($\approx H_2$) of it could have been present. This would represent but 0.09% of Fraction 4 and would escape identification by absorption in 83% sulfuric acid.

Experiment at 400°.—Data: butane used, 6.19 l.; rate of flow, 62 cc./min. Exit gas: volume 6.67 l.; rate of flow, 67 cc./min. Room temp., 25°. Volume of heated part of tube, 215 cc. Contact time, 1.5 minutes. Extent of decomposition, 2.6%.

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[6] Ethyl ether was avoided because of its low boiling point.

TABLE I

ANALYSIS OF GAS FROM PYROLYSIS OF n-BUTANE AT 415°

Fraction	1	2	3	4	Summary	
Distn. limits, °C.	−180 to −105	−105 to −50	−50 to −20	−20 to 0		
Volume, cc.	900	390	550	14,440	16,280	
	Analysis of each fraction, % by volume				Cc.	% (air-free basis)
Propylene	3.36	8.95	92.78	...	575	3.55
Ethylene	13.65	43.80	4.34	...	319	1.95
Oxygen	2.22	0.93	...	...	23	...
Hydrogen	1.42	...	...	...	13	0.70
Methane	69.20	...	...	...	623	3.86
Ethane	...	44.34	...	...	174	1.07
Butane	...	...	2.88	100.0	14,456	89.50
Nitrogen	9.81	1.98	...	...	97	...

The Podbielniak distillation of the reaction products revealed 81 cc. in the methane fraction, 118 cc. in the C_2 fraction, and 121 cc. in the propylene fraction. The C_2 fraction was composed as follows: ethylene, 60.2 cc.; ethane 56.2 cc.; propylene, 1.6 cc. Little interest attached itself to the methane and propylene fractions, but the identity of these substances was confirmed.

The 365°-Experiment.—In this run 62.9 g. (equivalent to 24.26 liters of gas at S. T. P.) of synthetic butane was distilled through the furnace at a uniform speed during 131 minutes. Thus, the rate of flow was 0.48 g./min. This is equivalent to 200 cc./min. at 25°. The contact time was 0.49 min. (vol. of tube, 215 cc.). These conditions were selected, especially the lower temperature, to ensure a very small extent of decomposition. Actually, it was 0.46%.

To facilitate the isolation of the more volatile reaction products, the unused butane was condensed in a flask at −80°; the uncondensed portion was collected separately. At the end of the experiment the butane condensate was distilled through a Davis column to recover any admixed C_2 and C_3 hydrocarbons. These were united with the original uncondensed portion and distilled through the Podbielniak column using liquid air. The first fraction (to −105°) was 84.6 cc. Besides methane, this consisted of 1.95 cc. of ethylene and a trace of hydrogen. The second fraction (−105 to −50°) was 87.1 cc. It contained 42.2 cc. of ethane, 40.8 cc. of ethylene and 4.1 cc. of propylene. For the purpose of this investigation, this second fraction was the important one. The third fraction (−50 to −20°) was 72.3 cc. It contained 1.5 cc. of ethylene and 70.8 cc. of propylene.

Thus, from the 24,260 cc. of original synthetic butane these totals of reaction products were isolated and identified, calculated to standard conditions: methane, 62.3 cc.; propylene, 67.4 cc.; ethane, 38.0 cc.; ethylene, 39.8 cc.

Summary

It has been demonstrated that the pyrolytic products from n-butane at incipient decomposition temperatures include ethane, ethylene and traces of hydrogen as well as methane and propylene. No evidence could be found to support the contention that there is scission at an exclusive C–C location in the molecule if temperatures near the "initial decomposition temperature" are used.

EVANSTON, ILLINOIS

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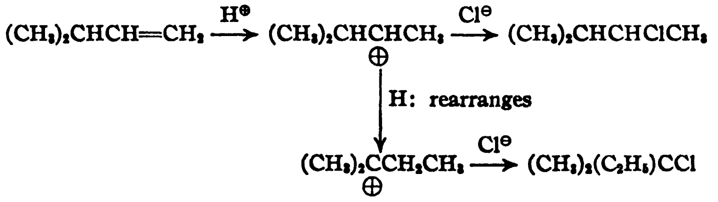
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Secondary Isoamyl Chloride, 3-Chloro-2-methylbutane

BY FRANK C. WHITMORE AND FRANKLIN JOHNSTON[1]

In the many preparations of this chloride,[2] it has invariably been accompanied by *tert*-amyl chloride. The implied or stated assumption has been that the secondary chloride was first formed and then rearranged to the tertiary chloride. Indeed, in the most recent work, Waterman states that the secondary chloride is unstable at its boiling point at atmospheric pressure. Other investigations in this Laboratory indicated that the secondary chloride should be stable and that the tertiary chloride was not formed by way of the secondary chloride.[3] The present study has confirmed these points. Hydrogen chloride was added to isopropylethylene at room temperature without any added catalyst according to the technique of Kharasch,[4] whereby peroxides and moisture are excluded. A 90% yield of an equimolecular mixture of secondary isoamyl chloride and tertiary amyl chloride resulted. The tertiary chloride was removed by hydrolysis with water at room temperature and the residual secondary chloride was dried and distilled at reduced pressure below 26°. The purified chloride was stable to long heating at 100°. Its structure was proved by conversion to methylisopropylcarbinol through the Grignard reaction.[5]

The course of the addition of hydrogen chloride to isopropylethylene, according to the working hypothesis used in this Laboratory,[3] would be as follows:



$$\begin{array}{l}(CH_3)_2CHCH{=}CH_2 \xrightarrow{H^{\oplus}} (CH_3)_2CH\underset{\oplus}{C}HCH_3 \xrightarrow{Cl^{\ominus}} (CH_3)_2CHCHClCH_3 \\ \qquad\qquad\qquad\qquad \downarrow \text{H: rearranges} \\ \qquad\qquad\qquad (CH_3)_2\underset{\oplus}{C}CH_2CH_3 \xrightarrow{Cl^{\ominus}} (CH_3)_2(C_2H_5)CCl\end{array}$$

It is notable that the "positive fragment" which undergoes rearrangement is not formed by the removal of an atom or group with a complete octet of electrons,[3] but is *formed by the addition of a proton to one carbon of the*

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[1] Submitted in partial fulfilment for the Ph.D. degree.

[2] Wurtz, *Ann.*, **129**, 368 (1864); Schorlemmer, *Ber.*, **7**, 1793 (1874); Wischnegradsky, *Ann.*, **190**, 328 (1878); Mayberry and Hudson, *Am. Chem. J.*, **19**, 243 (1897); Ipatiew and Dechanow, *Chem. Zentr.*, II, 691 (1904); Michael and Zeidler, *Ann.*, **385**, 227–292 (1911); Sabatier and Mailhe, *Compt. rend.*, **156**, 658 (1913); *ibid.*, **169**, 124 (1919); Aschan, *Chem. Abs.*, **14**, 3654 (1920); Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929); Pratesi, *Atti. Accad. Lincei*, **13**, 779 (1931); Piotrowski and Winkler, *J. Inst. Pet. Techn.*, **17**, 225–240 (1931); Leenderste, Tulleners and Waterman, *Rec. trav. chim.*, **52**, 515 (1933).

[3] Whitmore, THIS JOURNAL, **54**, 3274–3283 (1932); Fleming and Whitmore, *ibid.*, **54**, 3460 (1932); **55**, 4161 (1933).

[4] Kharasch and Mayo, *ibid.*, **55**, 2493 (1933).

[5] Whitmore and Lux, *ibid.*, **54**, 3448 (1932).

ethylenic linkage leaving the other carbon with only six electrons.[6] Several other cases of this phenomenon are being studied in this Laboratory.

Experimental

The Addition of Hydrogen Chloride to Isopropyl Ethylene.—The technique of Kharasch[4] was used. A typical run follows: isopropylethylene, b. p. 20–21° (745 mm.), from the dehydration of isoamyl alcohol over alumina, purified by treatment with sulfuric acid according to Wischnegradsky,[2] and dry hydrogen chloride were sealed in a Pyrex tube 60 × 3.1 cm. with 3-mm. wall. After seven weeks (optimum time not determined) in the dark at room temperature, the tube was opened with the proper precautions and the excess hydrogen chloride determined by allowing it to escape into scrubbing towers. Dissolved hydrogen chloride was removed by passing a stream of dry nitrogen through the chloride mixture cooled in an ice–salt bath. From 33 g. (0.47 mole) of isopropylethylene 44 g. (0.41 mole) of amyl chlorides was obtained; yield, 88%. There was an excess of 16 g. (0.44 mole) of hydrogen chloride.

Analysis of the Reaction Mixture.—The crude chloride mixture had n^{20}_{D} 1.4060 and d^{20}_{4} 0.866. Carius determinations showed 98.0–98.6% amyl chlorides.

A determination for tertiary chloride according to the method of Michael and Zeidler[2] was made by hydrolyzing a sample with a known quantity of water at room temperature. It was 48–48.5% hydrolyzed in one-half hour. Pure tertiary amyl chloride under the same conditions was 95% hydrolyzed.

Hydrolysis of the crude chloride with an excess of 0.1*N* silver nitrate for three hours at room temperature indicated only 56–57% tertiary and secondary chlorides. Hydrolysis during sixteen hours with silver nitrate gave 68–69%, and during sixty hours 95% secondary and tertiary. Primary isoamyl chloride under the latter conditions reacted only 3–4%. Therefore, the reaction mixture contained approximately equal amounts of the tertiary and secondary amyl chlorides.

Isolation of the Pure Secondary Isoamyl Chloride.—The reaction mixture was freed from tertiary amyl chloride by repeated hydrolyses with water until the wash water no longer gave a test for the chloride ion. The chloride was then dried over anhydrous sodium sulfate in the refrigerator.

Distillation was carried out at reduced pressure in a total condensing, indented, Pyrex Vigreux column 68 × 1.1 cm. the condenser and fraction cutter of which were cooled by circulating ice water. A spiral glass trap in a freezing mixture, an automatic pressure regulator, and a water pump completed the set up.

Fraction	Temp., °C.	n^{20}_{D}	Wt., g.	Press., mm.	Reflux ratio
Initial	23.4			60	
1	25.0	1.4080	3.5	60	15:1
2	25.4	1.4095	6.5	60	15:1
3	25.7	1.4095	13.5	60	20:1
4	25.8	1.4092	4.5	60	10:1
5	In trap	1.4075	5		
6	Residue		0.5		

In spite of the precautions for cooling the distillate about 20% of the original charge was lost during the fractionation.

Fraction 3 had d^{20}_{4} 0.878, MR$_D$ 30.03, calcd. 30.16.

Fractions 2–4 were combined and distilled from a modified Cottrell b. p. apparatus. The initial b. p. was 91.8° and after 80% had been distilled off the b. p. was 91.9° (736

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(6) *Cf.* Lowry, *J. Chem Soc.*, **123**, 3006 (1923).

mm.). No hydrogen chloride could be detected either by wet litmus paper or by odor. The pure chloride had a sweet odor similar to that of the other amyl chlorides.

Proof of the Structure of the Secondary Chloride.—Since Whitmore and Lux[6] have shown that there is no rearrangement during the conversion of an aliphatic halide to the corresponding alcohol by the Grignard reaction, this method was used to determine the structure of the secondary chloride.

To 1.2 g. (0.05 mole) of fine magnesium turnings with a crystal of iodine in a 200-cc. round-bottomed three-necked flask fitted with a stirrer, dropping funnel, and reflux condenser was added 5 g. (0.05 mole) of the dried secondary chloride (after removal of the tertiary chloride but without distillation) diluted with 10 cc. of dry ether after starting the reaction with 2–3 cc. of this mixture. No difficulty was encountered. The reaction mixture was allowed to stand overnight and treated with dry oxygen in the cold. The addition product was decomposed with ice and ammonium chloride in the usual manner, the aqueous layer extracted with 25 cc. of ether, the ether extracts dried with 1 g. of potassium carbonate, and the ether removed through the Vigreux column described above. Without further purification this carbinol gave an α-naphthyl urethan, m. p. 108–110° after three crystallizations from petroleum ether. The α-naphthyl urethan of a known sample of methylisopropylcarbinol had m. p. 111–112°, mixed m. p. 110–111°.

The 3,5-dinitrobenzoate was also prepared. It melted at 74–75° after three crystallizations from dilute ethyl alcohol. The 3,5-dinitrobenzoate of methylisopropylcarbinol had a m. p. 76°; mixed m. p. 74–75°.

Stability of the Secondary Chloride.—Four grams of the crude secondary chloride was heated in a sealed tube in live steam at atmospheric pressure for twenty-four hours. At the end of that time the chloride had become slightly yellow, but there was no odor of hydrogen chloride. A Grignard reaction was run as before, but considerable difficulty was experienced in starting the reaction. After treatment with oxygen and isolation of the carbinol as above, the 3,5-dinitrobenzoate of methylisopropylcarbinol was obtained, m. p. and mixed m. p. 74–75°.

Summary

1. Secondary isoamyl chloride, 3-chloro-2-methylbutane, has been prepared in pure form.
2. This chloride is stable at its boiling point at atmospheric pressure, stable at 100° for twenty-four hours, and stable to water at room temperature.
3. A new type of rearrangement resulting from addition to an olefinic linkage is indicated.

STATE COLLEGE, PENNSYLVANIA

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Studies of Polymerization and Ring Formation. XIX.[1] Many-Membered Cyclic Anhydrides

BY JULIAN W. HILL AND WALLACE H. CAROTHERS

Terminology.—To clarify the text of subsequent papers the following definitions are presented. Some of the terms here defined were first introduced in previous papers of this series,[2] but they have not yet gained very wide currency, while in some cases they have been used in a sense different from that suggested.

Linear Polymers, e. g.

$\ldots$—CH_2CH_2O—CH_2CH_2O—CH_2CH_2O—CH_2CH_2O—CH_2CH_2O—CH_2CH_2O—$\ldots$

are those whose molecules are built up from a recurring bivalent radical or *structural unit, e. g.*, —CH_2CH_2O—. Linear polymers are not necessarily open chains; they may be rings. *Superpolymers* are linear polymers having molecular weights above 10,000. The *unit length* is the number of atoms in the chain of the structural unit; in polyethylene glycol (or oxide) the unit length is three. *Macrocyclic compounds* are rings of more than seven atoms. *Monomers* are compounds containing only one structural unit; ethylene oxide and ethylene glycol are both monomers, since each has one —CH_2CH_2O— group. *Dimers* contain two units: dioxane and diethylene glycol are both dimers. *Bifunctional compounds* are chains bearing two groups capable of mutual reaction with the formation of a new bond. Bifunctional compounds always formally present two possibilities of self-reaction: *intramolecular* leading to ring closure, and *intermolecular* leading to chain formation.

Cyclic Anhydrides.—In previous papers, studies of adipic[3] and sebacic[4] anhydrides have been reported. The present paper describes the extension of these studies to the anhydrides of pimelic, suberic, azelaic, undecanedioic, dodecanedioic, brassylic, tetradecanedioic and octadecanedioic acids. The results closely resemble those already reported.

The anhydrides obtained by the action of acetic anhydride or acetyl chloride on the acids are linear polymers of the type formula —O—CO—R—CO—O—CO—R—CO—O—CO—R—CO—... These products are called α-anhydrides to distinguish them from other forms (β, γ, ω) that originate in other ways. They are very reactive, microcrystalline powders which are only slightly soluble in organic solvents and have molecular weights in the neighborhood of 3000 to 5000. They react with aniline to yield a mixture of the dianilide, the monoanilide, and the dibasic acid in the ratio 1:2:1.[3,4] This reaction serves to distinguish any sort of polymeric dibasic acid anhydride from the cyclic monomer, which yields exclusively with monoanilide.

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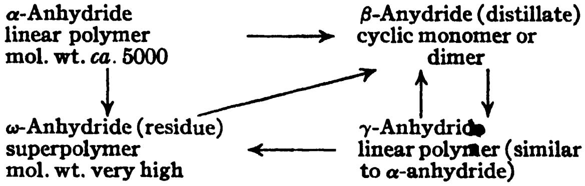
[1] An abstract of papers XIX, XX, XXI and XXII was presented at the Washington meeting of the American Chemical Society, March 28, 1933.

[2] Carothers, THIS JOURNAL, 51, 2548 (1929); Carothers, *Chem. Rev.*, 8, 353 (1931); Carothers and Hill, THIS JOURNAL, 54, 1559 (1932).

[3] Hill, *ibid.*, 52, 4110 (1930).

[4] Hill and Carothers, *ibid.*, 54, 1569 (1932).

When the α-anhydrides are heated in a high vacuum with a condenser placed close to the evaporating surface (molecular still),[5] they undergo the transformations summarized in the following scheme:



The α-anhydride yields β-anhydride and ω-anhydride simultaneously. As the β-anhydride collects on the condenser, the residue increases progressively in viscosity and molecular weight. The resulting ω-anhydride when cold is a very tough, opaque, solid; it becomes transparent (melts) at a definite temperature without flowing; and at still higher temperatures it can be drawn into pliable, highly oriented fibers.[6] The ω-anhydride depolymerizes just as the α-anhydride does, and if heating in the molecular still is continued long enough complete conversion to β-anhydride finally occurs. The β-anhydrides on being heated or allowed to stand readily revert to a polymeric form, the γ-anhydride. In their physical properties the γ-anhydrides are generally practically indistinguishable from the α-anhydrides. However, the latter structurally are probably open chains terminated by acetyl groups while the former at least when freshly formed under anhydrous conditions are perhaps giant rings.[4]

Adipic anhydride differs from the higher homologs in that the α-anhydride depolymerizes relatively easily even in an ordinary distillation apparatus. The other anhydrides differ from each other only in the nature of the volatile β-anhydride which they yield on depolymerization. The facts in this connection are shown in Table II. It will be observed that those anhydrides whose unit lengths are 7, 8, 10, 12, 14, 15 and 19 yield monomeric β-anhydrides and that those whose unit lengths are 9, 11 and 13 yield only dimeric β-anhydrides. These relations are represented graphically in Table I.

The three dimeric anhydrides (suberic, sebacic and dodecanedioic) are sharply crystalline solids sufficiently stable that their molecular weights can be determined cryoscopically in benzene. When allowed to react with aniline they furnish the dibasic acid, its monoanilide, and its dianilide in

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(5) *Cf.* Carothers and Hill, THIS JOURNAL, 54, 1557 (1932). The Washburn type of still was used in this work.

(6) Carothers and Hill, *ibid.*, 54, 1579 (1932).

TABLE I

NATURE AND STABILITY OF β-ANHYDRIDES

Dimers stable up to melting point		Unit length		Monomers Unstable			Monomers Extremely unstable
		7	(adipic) →	7			
		8	(pimelic) →			8	
18	← (suberic)	9					
		10	(azelaic) →				10
22	← (sebacic)	11					
		12	(undecanedioic) →				12
26	← (dodecanedioic)	13					
		14	(brassylic) →		14		
		15	(tetradecanedioic) →	15			
		⋮			•		
		19	(octadecanedioic) →	19			

the ratio 1:2:1. When heated above their melting points the dimeric anhydrides polymerize almost instantly to γ-anhydrides.

The monomeric anhydrides are not sufficiently stable to permit cryoscopic molecular weight determinations, but their identity as monomers is established by the fact that they react with aniline to yield pure monoanilide. The first and last members of the series are low-melting crystalline solids; the others are all liquids.

The monomers show characteristic differences in stability. Adipic β-anhydride, the seven-membered ring, polymerized completely in about seven hours at 100° under rigorously anhydrous conditions and fairly rapidly at room temperature in the presence of traces of moisture. The 8-, 10- and 12-membered monomers polymerize so rapidly even at very low temperature that a special technique was required to demonstrate their temporary existence. When distilled in the molecular still onto a condenser cooled by tap water, they condensed as transparent fluid drops, which in the course of an hour or less became opaque, and in several hours set to hard waxes. Distillate collected under these conditions invariably contained polymer, since its reaction with aniline always yielded dianilide. In the method devised, the condenser was cooled by means of liquid air. At this temperature the monomers condensed as solids. When, after several hours, a sufficient quantity of distillate had collected, a small reservoir of aniline (Fig. 1) was connected with the vacuum system by opening a stopcock, and a layer of crystalline aniline was deposited by evaporation on top of the anhydride distillate. The condenser was then allowed to warm up gradually, and as soon as the aniline started to melt, was quickly removed from the still and the lower part, bearing the distillate, was submerged in aniline. When the reaction was completed, the mixture was examined for dianilide and monoanilide.

When this method was applied to pimelic anhydride (8-atom unit) it yielded pure monoanilide. The next two members, azelaic and undecanedioic anhydrides (10- and 12-atom units) gave mixtures of acid, monoanilide and dianilide. However, the presence of some monomer in the distillate was established by the fact that the ratio of monoanilide was considerally higher than that required by the theory for dimer or other polymer. Moreover, when the condenser was operated at a higher temperature, these anhydrides first collected as transparent fluid drops with no evidence of the presence of crystalline material (dimer). It seems very probable therefore that the distillates were initially pure monomers and that the presence of dianilide in the aniline reaction product was due to subsequent polymerization.

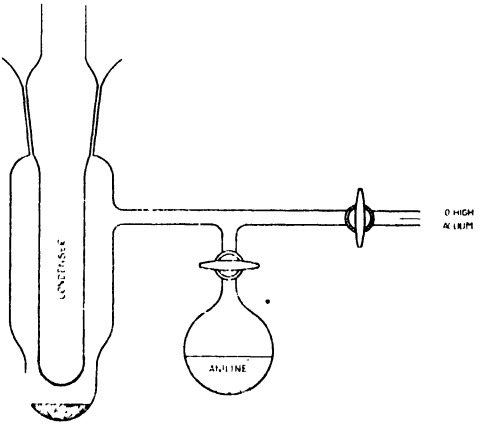

Fig. 1.

The next three members of the monomer series were much more stable than those of 10- and 12-atoms. Brassylic anhydride (14-atom unit) yielded pure monoanilide when the condenser was cooled with solid carbon dioxide and acetone. The liquid distillates from the 15- and 19-membered anhydrides (tetradecanedioic and octadecanedioic) when condensed at the temperature of tap water yielded pure monoanilide if allowed to react with aniline within a few hours of distillation. These two monomeric anhydrides, like that of adipic acid, could also be preserved for several days at room temperature without complete polymerization.

TABLE II

CYCLIC ANHYDRIDES

Acid	Structural unit of anhydride	Product of depolymerization and size of ring	Stability	M. p., °C.
Adipic	—OC$(CH_2)_4$CO—O—	Monomer 7	Unstable	20
Pimelic	—OC$(CH_2)_5$CO—O—	Monomer 8	Extremely unstable	Liq.
Suberic	—OC$(CH_2)_6$CO—O	Dimer 18	Stable up to m. p.	56–57
Azelaic	—OC$(CH_2)_7$CO—O	Monomer 10	Extremely unstable	Liq.
Sebacic	—OC$(CH_2)_8$CO—O	Dimer 22	Stable up to m. p.	68
Undecanedioic	—OC$(CH_2)_9$CO—O—	Monomer 12	Extremely unstable	Liq.
Dodecanedioic	—OC$(CH_2)_{10}$CO—O	Dimer 26	Stable up to m. p.	76–78
Brassylic	—OC$(CH_2)_{11}$CO—O—	Monomer 14	Unstable	Liq.
Tetradecanedioic	—OC$(CH_2)_{12}$CO—O—	Monomer 15	Unstable	Liq.
Octadecanedioic	—OC$(CH_2)_{16}$CO—O—	Monomer 19	Unstable	36–37

Experimental Part

Preparation of α-Anhydrides.—The α-anhydrides were prepared by the following method. A small quantity of the acid (5 to 20 g.) was refluxed with three parts by weight of acetic anhydride for four to six hours. In the case of the less soluble octadecanedioic acid six parts of acetic anhydride was used. The volatile material was distilled off under the vacuum of a water aspirator. The crude anhydrides were dissolved in hot dry benzene and precipitated, after filtration of the solutions, with petroleum ether. They were then preserved in a vacuum over potassium hydroxide, phosphorus pentoxide and paraffin. The α-anhydrides separate from solution as white microcrystalline powders. In the molten state they are very viscous liquids which crystallize on cooling in the form of small radiating clusters of microscopic needles and finally solidify to hard waxes.

TABLE III

ANALYTICAL DATA FOR α-POLYANHYDRIDES

α-Anhydride	Empirical formula	M. p., °C.	Analyses, %					
			Calcd.		Found			
			C	H	C		H	
Pimelic	$C_7H_{10}O_3$	53–55	59.11	7.11	...	...	...	...
Suberic	$C_8H_{12}O_3$	65–66	61.50	7.75	61.67	61.04	7.68	7.42
Azelaic	$C_9H_{14}O_3$	53–53.5	63.49	8.29	63.04	63.09	7.86	7.91
Undecanedioic	$C_{11}H_{18}O_3$	69–70	66.60	9.18	65.90	65.71	9.31	9.29
Dodecanedioic	$C_{12}H_{20}O_3$	86–87	67.86	9.52	66.88	67.01	9.63	9.84
Brassylic	$C_{13}H_{22}O_3$	76–78	68.97	9.81	68.80	68.98	9.96	10.05
Tetradecanedioic	$C_{14}H_{24}O_3$	89–91	69.94	10.08	69.17	69.32	9.94	9.79
Octadecanedioic	$C_{18}H_{32}O_3$	94–95	72.90	10.90	72.69	72.02	10.69	10.49

Reaction of the Anhydrides with Aniline.—A small sample of the anhydride (*ca.* 2 g.) was added to 5 to 10 cc. of aniline and triturated with a stirring rod until a smooth cream was formed. The mixture was then treated with 10% hydrochloric acid to dissolve the excess aniline, cooled and filtered. The mixtures derived from the anhydrides below undecanedioic were separated by treatment with boiling water, in which the dianilides are completely insoluble. The monoanilides separated from the filtrate on cooling. Sufficient water was used to keep the dibasic acids in solution. The separation of the mixtures from the anhydrides above sebacic was accomplished by means of dilute aqueous sodium hydroxide, which dissolved the monoanilide and the dibasic acids as sodium salts and left the dianilide. The monoanilide and the dibasic acid were precipitated from the filtered solution by acidification, and separated by means of boiling water. In the cases of tetradecanedioic and octadecanedioic anhydrides, the alkaline separation was carried out hot, as the sodium salts of these monoanilides are difficultly soluble in the cold. Up to and including undecanedioic α-anhydride, the dianilide was estimated quantitatively and in each case was obtained in 25% yield, as required by theory. A clean separation was difficult with the higher homologs as the alkaline solutions were increasingly soapy. The properties of the anilides are given in Table IV.

Depolymerization.—The molecular still (Fig. 1) used in these experiments was a cylindrical vessel, 18 cm. high and 5 cm. in diameter, with a rather flat curved bottom and an outlet to a high vacuum system. Into this vessel was fitted, by means of a large ground joint at the top, another cylinder 3 cm. in diameter, the rounded bottom of which was 3 cm. from the bottom of the larger vessel. This inner vessel constituted the condenser. A sample of α-anhydride was introduced into the outer vessel, the condenser was placed in position and the apparatus was evacuated by means of a mercury diffusion pump backed by a Hyvac oil pump. A trap cooled by solid carbon dioxide in acetone was placed in the system. The still was heated by means of a metal bath.

TABLE IV

MONOANILIDES

	M. p., °C.	Cryst. from	Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C		Found H	
Pimelic	108–109	H_2O	$C_{13}H_{17}O_3N$	66.35	7.27	66.23		7.55	
Suberic	128–129	Benzene	$C_{14}H_{19}O_3N$	67.42	7.70	67.51		7.86	
Azelaic	107–108	Dil. EtOH	$C_{15}H_{21}O_3N$	68.39	8.05	68.05	68.32	7.89	8.02
Undecanedioic	112.5–113	50% EtOH	$C_{17}H_{25}O_3N$	70.06	8.65	70.28	70.10	8.94	9.03
Dodecanedioic	123	50% EtOH	$C_{18}H_{27}O_3N$	70.77	8.91	70.85	71.13	8.96	8.72
Brassylic	118.5–119.5	50% EtOH	$C_{19}H_{29}O_3N$	71.41	9.18	71.71	71.46	9.60	9.37
Tetradecanedioic	124–125	60% EtOH	$C_{20}H_{31}O_3N$	72.01	9.39	71.97	72.27	9.42	9 10
Octadecanedioic	128–129	60% EtOH	$C_{24}H_{39}O_3N$	73.98	10.10	74.15	74.09	10.02	9.92
			DIANILIDES						
Pimelic	155–156	MeOH–H_2O	$C_{19}H_{22}O_2N_2$	73.50	7.16	73.16		7.11	
Suberic	186–187	MeOH	$C_{20}H_{24}O_2N_2$	74.03	7.46	73.87	73.95	7.52	7.29
Azelaic	186–187	Xylene	$C_{21}H_{26}O_2N_2$	74.51	7.75	74.03		7.94	
Undecanedioic	160–161	EtOH	$C_{23}H_{30}O_2N_2$	75.35	8.27	75.44	75.32	8.28	8.44
Dodecanedioic	170–171	EtOH	$C_{24}H_{32}O_2N_2$	75.73	8.49	76.28	76.09	8.47	8.46
Brassylic	160–161	EtOH	$C_{25}H_{34}O_2N_2$	76.08	8.70	75.86	76.16	8.84	8.74
Tetradecanedioic	169.5–170	EtOH	$C_{26}H_{36}O_2N_2$	76.41	8.89	76.41		8.91	
Octadecanedioic	162–163	EtOH	$C_{30}H_{44}O_2N_2$	77.52	9.56	77.38	77.64	9.76	9.78

Pimelic Anhydride.—The α-anhydride was heated at 150°. The β-anhydride collected on the water-cooled condenser as a dew which solidified to a pasty gel in about one hour and to a hard wax overnight (γ-anhydride). The saponification equivalent of the wax was 70.7 [$(C_7H_{10}O_3)_n$ requires 71.0]. The experiment was repeated with liquid air in the condenser and the heating bath at 125°. The heating was continued for six hours, after which the still was isolated from the vacuum system by closing a stopcock and put in communication with a small evacuated bulb containing aniline by opening a stopcock (see Fig. 1). Aniline was distilled into the still until a layer of crystalline aniline completely covered the distillate on the condenser. To accomplish this, it was necessary to let the liquid air evaporate almost completely from the condenser. The liquid air was finally allowed to evaporate completely. As soon as the condenser had warmed up to a point where the aniline started to melt, the vacuum was relieved and the condenser removed and immersed in aniline to a level slightly above the coating of distillate. When the mixture had come to room temperature, it was treated with dilute hydrochloric acid. Complete solution indicated the absence of any dianilide in the reaction product. The solution was made alkaline and extracted three times with ether. It was then concentrated and acidified to Congo Red. The precipitate was filtered off and treated carefully with cold water to remove sodium chloride. The residue of monoanilide was recrystallized from water; m. p. 107–108. It did not depress the melting point of an authentic sample of melting point 108–109°. The absence of any dianilide in the aniline reaction product demonstrates that the β-anhydride was monomeric.

Suberic Anhydride.—A sample of α-anhydride was heated at 160° in the molecular still. The β-anhydride collected as a crystalline solid on the water-cooled condenser at the rate of about 0.1 g. a day. It melted at 55–57°. This compound proved to be the cyclic dimer of suberic anhydride.

Anal. Calcd. for $C_{16}H_{24}O_6$: C, 61.50; H, 7.75; mol. wt., 312.2; saponification equiv., 78.0. Found: C, 61.57, 61.67; H, 7.72, 7.89; mol. wt. (cryoscopic in benzene), 343, 355, 346; saponification equiv., 77.5.

It reacted with aniline to form the monoanilide (m. p. 125–127°) and the dianilide (m. p. 186–187°) of suberic acid, which were identified by mixed melting points. When heated above its melting point it rapidly polymerized to the γ-anhydride, a waxy solid melting at 65–68°; mol. wt. observed in boiling benzene, 703, 718.

Azelaic Anhydride.—The α-anhydride was heated in the molecular still at 150°. The β-anhydride collected on the water-cooled condenser as a liquid and soon solidified to a gel and then in about twelve hours to a wax (γ-anhydride). The observed saponification equivalent of the wax was 84.8, and 84.5 [$(C_9H_{14}O_3)_x$ requires 85]. Two runs were made in which the condenser was cooled with liquid air and the cold distillate was treated with aniline as described under pimelic anhydride, but products free of dianilide were not obtained. The amounts of the two anilides were determined quantitatively, taking advantage of the insolubility of the dianilide in hot water and the insolubility of the monoanilide in cold.

(*1*) *Four hours:* Dianilide, 0.18 g.; monoanilide, 0.35 g.—A polymeric anhydride yields 2 moles of monoanilide for one of dianilide; a monomeric anhydride yields only monoanilide. The dianilide found indicates an amount of polyanhydride that could produce only 0.28 g. of monoanilide. The excess, 0.07 g., must arise from monomeric anhydride, and this amount corresponds with 11% of monomer in the total anhydride sample.

(*2*) *Six hours:* Dianilide, 0.22 g., equivalent to 0.34 g. of monoanilide (from polyanhydride). Monoanilide found, 0.49 g.; excess due to monomeric anhydride, 0.15 g., equivalent to 18% of monomer in the total anhydride sample.

Since there was no evidence of any dimer (which should be a crystalline solid) in the distillate, the failure to demonstrate that the distillate was initially pure monomer was probably due to the fact that the latter polymerized to a considerable extent before the examination could be completed.

The distillate if removed when still liquid or pasty, had a spicy, aromatic odor. This disappeared when the distillate solidified completely.

1,11-Undecanedioic Anhydride.—The α-anhydride was heated in the molecular still with a water-cooled condenser. The β-anhydride condensed first as a dew which soon became pasty and finally after a few hours set to a hard wax, m. p. 85–88°. Before complete solidification it had a spicy odor. The saponification equivalent of the wax was 98.8 [$(C_{11}H_{18}O_3)_n$ requires 99.1]. The experiment was repeated using liquid air in the condenser and the aniline technique described under pimelic anhydride. As the reaction product was found to contain dianilide, the amounts of dianilide and monoanilide formed were estimated quantitatively. The product from the aniline reaction was treated with a slight excess of warm dilute aqueous sodium hydroxide and the insoluble dianilide was filtered off and weighed (0.079 g.). The filtrate was acidified, cooled and filtered (weight of crystalline precipitate 0.281 g.). This material was shown by a determination of the neutralization equivalent to be pure monoanilide (calcd. 291; found, 289). The dianilide found (0.079 g.) indicates an amount of polymeric anhydride capable of yielding only 0.125 g. of monoanilide. The excess of the latter (0.156 g.) must have come from monomeric anhydride, and calculation indicates 38% of monomeric anhydride in the mixture.

1,12-Dodecanedioic Anhydride.—The α-anhydride was heated in the molecular still at 110°. A beautifully crystalline distillate of melting point 76–78° collected on the condenser at the rate of about 0.1 g. in two days. This β-anhydride was identified as the cyclic dimeric anhydride of dodecanedioic acid.

Anal. Calcd. for $C_{24}H_{40}O_6$: C, 67.86; H, 9.52; mol. wt., 424.4; saponification equiv., 106.1. Found: C, 67.15, 67.54; H, 9.46, 9.60; mol. wt. (cryoscopic in benzene), 496, 450; saponification equiv., 105.5.

It polymerized at the melting point and then melted again at 85–87°. It reacted with aniline in the usual way to yield monoanilide of m. p. 123° and dianilide of m. p. 169–170°.

Brassylic Anhydride.—The α-anhydride was heated in the molecular still for four hours at 150° with the condenser cooled with solid carbon dioxide and acetone. The distillate of β-anhydride was shown to be pure monomer by its reaction with aniline. The product was completely soluble in dilute aqueous sodium hydroxide. The monoanilide separated on acidification of the alkaline solution and was recrystallized from 50% alcohol. It melted at 118.5–119.5° and showed no depression when mixed with an authentic sample.

When the depolymerization of the anhydride was carried out using a water-cooled condenser, the β-anhydride collected as a liquid which changed in the course of a day to a pasty mass and in the course of two days to a hard wax (saponification equivalent found 112.7, calculated 113.1). The liquid was fragrant and aromatic and when allowed to react with aniline shortly after distillation yielded only a small amount of dianilide. The odor disappeared during the change to the wax.

1,14-Tetradecanedioic Anhydride.—The α-anhydride was heated four and one-half hours at 145–150° in the molecular still using solid carbon dioxide in acetone as the refrigerant in the condenser. The distillate of β-anhydride was shown to be pure monomer by its reaction with aniline. The product was completely soluble in a large volume of warm, dilute sodium hydroxide and consequently consisted of monoanilide free of dianilide. The monoanilide separated on acidification of the alkaline solution and was recrystallized from 60% alcohol. It melted at 124–125° and did not depress the melting point of an authentic sample.

When the depolymerization of the anhydride was carried out using a water-cooled condenser, the distillate, like that from brassylic anhydride, collected as a liquid which changed in the course of a day to a pasty mass and in the course of two to a hard wax, m. p. 88–91°. The distillate, before it changed completely to the hard wax, possessed a strong odor like that of musk. This odor was completely lost on saponification (saponification equivalent found, 120.4, 119.1; calcd., 120.1) and on heating to 100° which brought about the change to the γ-anhydride instantly.

1,18-Octadecanedioic Anhydride.—The behavior of this α-anhydride was identical in every respect with that of tetradecanedioic anhydride. The fresh liquid distillate likewise possessed the odor of musk but was rather fainter. It polymerized instantly on being heated to 100°, to a wax of m. p. 98–100° (γ-anhydride), losing its odor in the change. About 1 cc. of β-anhydride was collected using a still adapted for the collection of liquids. It crystallized on chilling or seeding and melted at 36–37° (saponification equivalent found, 146.5; calcd. for $C_{18}H_{32}O_3$, 148.1). After two weeks it had changed to the wax of m. p. 98-100°.

Summary

Data are presented on the anhydrides of dibasic acids $COOH(CH_2)_n$-COOH where n is 4, 5, 6, 7, 8, 9, 10, 11, 12 and 16. The anhydrides are all linear polymers and when heated in a molecular still they are depolymerized yielding volatile products (β-anhydrides). The latter are either cyclic monomers or dimers depending upon the unit length, $n + 3$. The compounds thus obtained are rings of 7, 8, 18 (dimeric), 10, 22 (dimeric), 12, 26 (dimeric), 14, 15 and 19 atoms. The dimers are crystalline solids which polymerize instantly when heated above their melting points. The monomers are liquids or low melting solids which polymerize at lower temperatures than the dimers. The monomers of 8, 10 and 12 atoms are exceedingly unstable and polymerize rapidly even below room temperature.

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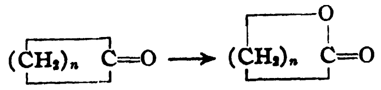
Studies of Polymerization and Ring Formation. XX. Many-Membered Cyclic Esters

BY JULIAN W. HILL AND WALLACE H. CAROTHERS

The only generally applicable method known for the synthesis of macrocyclic esters consists in oxidation of cyclic ketones with Caro's acid. This



I II (n = 12, 13, 14, 15, 16)

method, discovered by Baeyer and Villiger,[1] has been applied by Ruzicka and Stoll[2] to the synthesis of the lactones, II.

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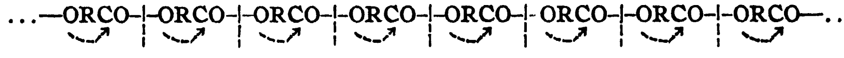
(1) Baeyer and Villiger, *Ber.*, **32**, 3625 (1899).

(2) Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

The reaction is far from clean-cut, while the requisite ketones (I) are obtained in yields not exceeding 5%.[3] The necessity for adopting this devious and extravagant method for synthesizing macrocyclic lactones is due to the fact, repeatedly illustrated in previous papers[4] of this series, that bifunctional esterifications involving unit lengths greater than seven yield almost exclusively linear polyesters instead of the desired cyclic esters. When linear polyesters of unit length greater than seven are heated, *e. g.*, to 275°, there is generally no evidence of depolymerization or distillation,[5] but at temperatures somewhat above 300° destructive general decomposition occurs, and from the complicated mixture of distillable products in four cases[6] true depolymerization products have been isolated. These cyclic esters however are not monomers but dimers, and the yields are very poor (5% or less).

When linear polyesters of unit length greater than seven are heated (*e. g.*, to 200–250°) under the conditions of molecular distillation,[7] the long chains couple to form still longer chains.[8] The products (superpolyesters) have molecular weights above 10,000 and are capable of being drawn out into tough, pliable, highly oriented fibers.[9]

It was recognized in advance that the conditions of the molecular still at high temperature would be likely to favor either this type of coupling or a depolymerization by ester interchange:[10]



...—ORCO-|-ORCO-|-ORCO-|-ORCO-|-ORCO-|-ORCO-|-ORCO-|-ORCO—...

Evidences of such depolymerization, at least in traces, were in fact frequently observed in the formation of superpolyesters, and after methods had been developed for the smooth depolymerization of polyanhydrides, attention was again turned to the polyesters. The result was the development of the method presently described by means of which it became possible to prepare with good yields and without unreasonable difficulty a whole series of macrocyclic esters, both monomeric and dimeric. Briefly,

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(3) Since this paper was prepared for publication Ziegler, Eberle and Ohlinger [*Ann.*, **504**, 94 (1933)] have described an ingenious method based on Ruggli's dilution principle for the preparation of large cyclic ketones in good yields. This principle has been referred to in previous papers of the present series [*e. g.*, THIS JOURNAL, **51**, 2551 (1929)] and we hope to describe its application to the synthesis of cyclic esters in future papers.

(4) Carothers, THIS JOURNAL, **51**, 2548 (1929); Carothers and Arvin, *ibid.*, **52**, 711; Carothers, Arvin and Dorough, *ibid.*, 3292; Carothers, *Chem. Reviews*, **8**, 353 (1931). *Cf.* Chuit and Hausser, *Helv. Chim. Acta*, **12**, 463 (1929); Lycan and Adams, THIS JOURNAL, **51**, 625, 3450 (1929).

(5) Compounds of molecular weight higher than 1000 cannot be distilled even under the highest vacua, Carothers, Hill, Kirby and Jacobson, THIS JOURNAL, **52**, 5279 (1931).

(6) The cases referred to are ethylene succinate, Tilitschejew, *J. Russ. Phys.-Chem. Soc.*, **57**, 143 (1925); Carothers and Dorough, THIS JOURNAL, **52**, 711 (1930); tetramethylene carbonate, Carothers and Van Natta, *ibid.*, **52**, 314 (1930); trimethylene oxalate, Tilitschejew, *J. Russ. Phys.-Chem. Soc.*, **58**, 447 (1926); Carothers, Arvin and Dorough, THIS JOURNAL, **52**, 3292 (1930); self-ester of hydroxydecanoic acid, Lycan and Adams, *ibid.*, **51**, 625, 3450 (1929).

(7) Carothers and Hill, *ibid.*, **54**, 1557 (1932).

(8) *Ibid.*, p. 1559.

(9) *Ibid.*, p. 1579.

(10) *Cf.* the discussion of 6-membered cyclic esters and their polymers in Carothers, Dorough and Van Natta, *ibid.*, **54**, 761 (1932).

the method consists in heating linear polyesters *in vacuo* at a temperature just below the point of thermal destruction under conditions that permit any volatile product to be removed by distillation as fast as it is formed.

The success of the new method, practically, depends upon numerous factors not all of which have yet been completely isolated and defined; the two most important however are the identity of the polyester and the use of catalysts. On the first point it may be said that esters of carbonic acid and of oxalic acid depolymerize more readily and smoothly than any others yet examined. On the second point, ester interchange catalysts (*e. g.*, sodium added as metal in the preparation of the initial polyester) are almost indispensable.

After some experimentation it was discovered that esters of carbonic acid and of oxalic acid can be depolymerized merely by heating them (with catalyst) under diminished pressure in an ordinary distilling flask. Most of the experiments now reported were however made in a simplified molecular still (described below) operated at pressures ranging from 0.1 to 2 or 3 mm.

The depolymerization of the polyester in favorable cases progresses smoothly and fairly rapidly, the cyclic ester distilling to the condenser and being collected as it is formed. The residual ester at the same time progressively increases in viscosity (formation of superpolymer); if this increase in viscosity does not proceed too far, depolymerization still continues and is ultimately almost complete and quantitative. In many cases however the residue, before complete depolymerization, becomes converted to a gel; even at 250° it is completely immobile and resembles a piece of porous, vulcanized, gum rubber. Depolymerization then practically ceases. This residue incidentally is extraordinarily resistant to attack by solvents and chemical agents generally. It evidently results from a polymerization which has progressed beyond the linear superpolymer stage. It seems likely that some quantitatively minor side-reaction (dehydrogenation at a venture) occurs permitting accessory polymerization to form a three-dimensional macromolecule.

The product of the depolymerization is generally a mixture of cyclic monomer and cyclic dimer although in many cases one of these forms predominates to the practical exclusion of the other. The ratio of the two forms is in some cases quite sensitive to the experimental conditions (temperature, pressure, shape of apparatus) but the data on this point recorded in Table I were all obtained under closely similar conditions.

Preparation of Polyesters.—Polymeric carbonates derived from the glycols $HO(CH_2)_nOH$ where *n* is 3, 4, 6 and 10 and from diethylene glycol have already been described.[11] The new polymeric carbonates prepared as intermediates in the present work include those derived from the glycols $HO(CH_2)_nOH$ where *n* is 5, 7, 8, 9, 11, 12, 13, 14 and 18, and from

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[11] Carothers and Van Natta, THIS JOURNAL, 52, 314 (1930).

TABLE I

NATURE AND PHYSICAL PROPERTIES OF CYCLIC ESTERS

	Unit length	Proportions of monomer and dimer in distillate	M. p. of monomer, °C.	B. p. of monomer, °C.	n_D of monomer	d_4 of monomer	M. p. of dimer, °C.
Ethylene carbonate	5	Exclusively monomer	39	238	1.4158 (50°)	1.3079 (50°)	
Trimethylene carbonate	6	Exclusively monomer	47–48	135 at 4 mm.	1.4409 (50°)	1.2282 (50°)	
Tetramethylene carbonate	7	Mixture of dimer and tetrahydrofuran					175–176
Pentamethylene carbonate	8	Exclusively dimer					117–118
Hexamethylene carbonate	9	Almost exclusively dimer; odor of monomer					128–129
Heptamethylene carbonate	10	Almost exclusively dimer; odor of monomer					97–98
Octamethylene carbonate	11	Almost exclusively dimer; odor of monomer	21.5–23	74– 76 at 0.5 mm.	1.4665 (20°)	1.0727 (20°)	116–117
Nonamethylene carbonate	12	Almost exclusively dimer; odor of monomer	34–35	63– 64 at 0.1 mm.	1.4528 (50°)	1.0240 (50°)	95–95.5
Decamethylene carbonate	13	Mixture of monomer and dimer	10–11	92– 93 at 1 mm.	1.4659 (20°)	1.0354 (20°)	105–106
Undecamethylene carbonate	14	Mixture of monomer and dimer	40–41	104.5 at 7 mm.	1.4544 (50°)	0.9968 (50°)	97–97.5
Dodecamethylene carbonate	15	Almost exclusively monomer; small amount of dimer identified	11–12	118–119 at 3 mm.	1.4639 (20°)	1.0036 (20°)	93–95
Tridecamethylene carbonate	16	Almost exclusively monomer; no dimer isolated	23–24.5	149–150 at 4.5 mm.	1.4622 (25°)	0.9888 (25°)	
Tetradecamethylene carbonate	17		21–22	144–146 at 2 mm.	1.4622 (20°)	0.9814 (20°)	
Octadecamethylene carbonate	21		36–37	165–169 at 1 mm.	1.4537 (50°)	0.9273 (50°)	
Triethylene glycol carbonate	11	Mixture of monomer and dimer	Liq.				
Tetraethylene glycol carbonate	14	Exclusively monomer	42–44	128–130 at 1 mm.	1.4569 (50°)	1.1961 (50°)	
Decamethylene oxalate	14	Exclusively monomer	Liq.	125–126 at 0.2 mm.	1.4730 (20°)	1.0812 (20°)	
Undecamethylene oxalate	15	Exclusively monomer	23–24.5	120–123 at 0.5 mm.	1.4700 (25°)	1.0623 (25°)	
Decamethylene malonate	15	Exclusively monomer	Liq.	117–118 at 0.5 mm.	1.4695 (20°)	1.0599 (20°)	
Decamethylene succinate	16	Almost exclusively dimer; no monomer isolated					108–109
Ethylene sebacate	14	Almost exclusively dimer; trace of monomer isolated	40–41				80–81
Ethylene undecanedioate	15		35				143
Ethylene dodecanedioate	16	Almost exclusively dimer; no monomer isolated					95–96
Ethylene brassylate	17						145–146
Ethylene tetradecanedioate	18						102–103
Trimethylene sebacate	15						108–110
Self ester of ω-hydroxypentadecanoic acid	16	Almost exclusively dimer; odor of monomer	31–32[a]				83–84

[a] Ruzicka and Stoll, *Helv. Chim. Acta*, 11, 1159 (1928).

diethylene and triethylene glycols. The fact that these compounds are lacking in crucial physical properties (*e. g.*, sharply characteristic melting points) makes it unnecessary to describe them individually. They are all insoluble in water and soluble in certain organic solvents such as chloroform. They separate from solvents in the form of soft powders (microcrystalline). The molten polyesters are very viscous liquids which crystallize on cooling in the form of small radiating clusters of microscopic needles or spherulites and finally solidify to more or less hard, tough waxes. The polymeric carbonate derived from triethylene glycol, however, failed to solidify and was obtained only as a thick sirup.

The general method of preparation used for the new polycarbonates was the same as that already described,[11] but, on account of the boiling points involved, dibutyl carbonate was found to be a more convenient source of the acid radical than diethyl carbonate. To the mixture of glycol and alkyl carbonate a small amount of sodium was added; the mixture was heated at 170–220° until the distillation of alcohol ceased, and removal of the alcohol was completed by continuing the heating for two hours or more in vacuum. The residue was usually depolymerized without any purification. The alkylene oxalates and malonates were prepared from the glycols and the diethyl esters of the acids in the same manner as the carbonates. The other esters were prepared directly from the acids and the glycols.

Depolymerization.—The apparatus used in the depolymerizations for which data are listed in Table I consisted simply of a 250-cc. Pyrex suction filter flask. Through a rubber stopper in the neck of the flask was inserted a test-tube about 1.5 cm. in diameter. Its bottom was about 3 cm. distant from the bottom of the flask. The outside of this test-tube served as the condenser and receiver; the inside was cooled with a stream of tap water (in some cases a mixture of solid carbon dioxide and acetone); the distillate collected on the outside. At intervals the test-tube was removed and the solid or pasty distillate was scraped from it. When the distillate was sufficiently fluid to flow, a small glass thimble was hung on the end of the test-tube to catch the drip.

The side-tube of the flask was connected to a vacuum line. This line was connected to an oil pump and the pressure in the line was about 0.1 to 2 mm. No attempt was made to secure an exceedingly high vacuum. The flask was immersed to a depth of about 2 cm. in a metal bath which was kept at 210–240° by means of an electric heater.

Nature of the Depolymerization Products.—For the sake of completeness Table I includes the physical constants of ethylene and trimethylene carbonates. The former, a 5-atom ring, is known only as the monomer; the latter, which has a unit length of 6 atoms, can be obtained either as monomer or polymer, but the polymer depolymerizes so rapidly and smoothly on distillation that the use of a molecular still is quite unnecessary.[11]

The rest of the compounds listed in Table I are obtained by the ordinary methods of preparation only as linear polyesters; and the polyesters were all depolymerized in the apparatus and under the conditions described above.

The behavior of tetramethylene carbonate (7-atom unit) was exceptional: the distillate was found to contain a considerable amount of tetrahydrofuran, which obviously might arise by the loss of carbon dioxide from the structural unit. The chief product, however, was the dimer, a 14-membered ring which has already been described.[11] No detectable amount of monomeric ester was formed. The products from the next five members of the series (unit lengths 8 to 12 atoms) also were chiefly dimeric. Pentamethylene carbonate (8-atom unit) gave no detectable amount of monomer. The presence of some monomer in the distillate from hexamethylene carbonate was inferred from the odor, but the attempt to obtain isolable amounts of monomer by carrying out the depolymerization in ordinary distillation equipment gave only indefinite unsaturated products. The odors of the distillates from heptamethylene, octamethylene and nonamethylene carbonates also indicated the presence of monomer, and in the last two of these cases monomer was actually isolated and identified when the depolymerization was carried out in ordinary distillation equipment.

The next member of the series, decamethylene carbonate, showed a sharp change in the nature of the depolymerization products: considerable amounts of the monomer were formed even in the molecular still. Undecamethylene carbonate (14-atom unit) behaved similarly. Beyond this point the ratio was reversed: dodecamethylene carbonate (15-atom unit) gave only a small amount of dimer, and with higher members of the carbonate series the isolated products were exclusively monomeric.

The oxalates (decamethylene and undecamethylene) showed a greater tendency to yield monomers than did the carbonates of the same unit length. Decamethylene malonate also gave almost exclusively the monomer.

The rest of the compounds listed in Table I, compared with the carbonates, exhibited a peculiar reluctance toward the formation of monomers. Even ethylene tetradecanedioate yielded a 36-membered dimer and no appreciable amount of the 18-membered monomer. Similarly ω-hydroxypentadecanoic acid yielded the 32-membered dimer instead of the 18-membered monomer which has already been obtained by oxidation of the corresponding cyclic ketone.[12] It should be added that the depolymerization of all the esters referred to in this paragraph is especially slow and difficult. Depolymerization of carbonates, oxalates, and even malonates, proceeds much more rapidly and completely.

Effect of Conditions on the Ratio of Monomer to Dimer.—The data on the carbonates listed in Table I indicate that polyesters of this series on depolymerization yield dimers almost exclusively when the unit length is 7 to 12 inclusive, both monomer and dimer when the unit length is 13 and 14, and monomers almost exclusively when the unit length is more than 14. It will be shown later that this characteristic change in the

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(12) Ruzicka and Stoll, *Helv. Chim. Acta*, 11, 1159 (1928).

nature of the products under a given set of conditions is probably due to stereochemical factors inherently associated with the structure of the cyclic esters. It is also true, however, that the ratio of monomer to dimer can be controlled within certain limits by the experimental conditions. Thus octamethylene and nonamethylene carbonates in the modified molecular still yield almost exclusively the cyclic dimers, but when the depolymerization is conducted in an ordinary distilling flask the product is almost entirely the monomer. The distilling flask (unlike the molecular still) permits refluxing, so that while most of the monomer escapes most of the dimer is returned to the residue, where it is either cracked to monomer or converted to higher polymer. Limitations of this method of experimental control are indicated by the fact that when it was applied to hexamethylene carbonate no smooth depolymerization occurred and only indefinite unsaturated products were obtained. Esters of dibasic acids above malonic also depolymerize very slowly if at all in an ordinary distilling flask.

The depolymerization of polymeric decamethylene carbonate in an ordinary distilling flask gave a much higher yield of monomer than dimer and the examination of a large sample of crude product showed the presence of a by-product, decen-9-ol-1, $CH_2{=}CH(CH_2)_7CH_2OH$. The following data are typical.

The depolymerization was conducted in ordinary distilling flasks in batches of various sizes up to 100 g. and at (bath) temperatures up to 290°. The product was a mixture of colorless liquid and crystalline material. The crystals (a mixture of dimeric carbonate and decamethylene glycol) were removed by filtration, and the filtrate (2425 g.) was distilled, yielding 1276 g. of pure monomer, 400 g. of crystalline residue (chiefly dimer) and 742 g. of low-boiling material. The latter by redistillation was separated into four fractions of which the two largest were: A, b. p. 76–81° (2 mm.), 81%, and B, b. p. 87–89° (2 mm.), 9%. The latter was practically pure monomer. Analytical data for B indicated that it was a mixture of decamethylene carbonate (monomer) and decenol (apparently a constant-boiling mixture). The ester was destroyed by saponification with alcoholic sodium hydroxide, and the recovered alcohol was purified by distillation.

Decen-9-ol-1.—B. p. 85–86° (2 mm.); n_D^{20} 1.4480; d_4^{20} 0.8446; M_D calcd., 49.53; M_D found, 49.45.

Anal. Calcd. for $C_9H_{18}O$: C, 76.9; H, 12.8. Found: C, 76.51; H, 13.09.

Its structure was established by the fact that it was oxidized to azelaic acid by neutral aqueous permanganate (in one experiment a small amount of suberic acid was found) and hydrogenated to decanol-1 which was identified by comparison of the phenylurethan with a known specimen (crys. from 80% alcohol, m. p. 61–62°).

Decen-9-ol-1 yields a phenylurethan of m. p. 49–50° (crys. from 80% alcohol).

Polymerization of Macrocyclic Esters.—Macrocyclic esters, unlike 6-membered cyclic esters,[11] show no tendency to polymerize spontaneously. They do, however, polymerize at elevated temperatures especially in the presence of catalysts for ester-interchange, and the following observations are typical.

TABLE II

ANALYSIS OF CYCLIC ESTERS

Compound	Calculated, % C	H	Mol. Wt.	Found, % C	H	Mol. wt. in freezing benzene
Pentamethylene carbonate *dimer* $[-(CH_2)_5OCOO-]_2$	55.4	7.7	260	55.4	8.3	258 (b. p.)
Hexamethylene carbonate *dimer* $[-(CH_2)_6OCOO-]_2$	58.3	8.3	288	58.2	8.4	284 286
Heptamethylene carbonate *dimer* $[-(CH_2)_7OCOO-]_2$	60.8	8.9	316	61.2	8.9	313 312 (b. p.)
Octamethylene carbonate *monomer* $[-(CH_2)_8OCOO-]$	62.8	9.3	172	62.2	9.4	174
Octamethylene carbonate *dimer* $[-(CH_2)_8OCOO-]_2$	62.8	9.3	344	63.2	9.6	325 329 (b. p.)
Nonamethylene carbonate *monomer* $[-(CH_2)_9OCOO-]$	64.5	9.7	186	64.8	9.9	171
Nonamethylene carbonate *dimer* $[-(CH_2)_9OCOO-]_2$	64.5	9.7	372	64.6	9.7	330 329 (b. p.)
Decamethylene carbonate *monomer* $[-(CH_2)_{10}OCOO-]$	66.0	10.0	200	66.3	10.1	216 204
Decamethylene carbonate *dimer* $[-(CH_2)_{10}OCOO-]_2$	66.0	10.0	400	66.4	10.1	395 391
Undecamethylene carbonate *monomer* $[-(CH_2)_{11}OCOO-]$	67.3	10.3	214	67.5	10.3	213 211
Undecamethylene carbonate *dimer* $[-(CH_2)_{11}OCOO-]_2$	67.3	10.3	428	67.2	10.4	400 409
Dodecamethylene carbonate *monomer* $[-(CH_2)_{12}OCOO-]$	68.4	10.5	228	68.2	10.6	249 223
Dodecamethylene carbonate *dimer* $[-(CH_2)_{12}OCOO-]_2$	68.4	10.5	456	68.2	10.4	
Tridecamethylene carbonate *monomer* $[-(CH_2)_{13}OCOO-]$	69.4	10.7	242	69.2	10.5	265 238
Tetradecamethylene carbonate *monomer* $[-(CH_2)_{14}OCOO-]$	70.3	10.9	256	69.6	10.9	242 242
Octadecamethylene carbonate *monomer* $[-(CH_2)_{18}OCOO-]$	73.1	11.5	312	73.3	11.8	268 273 (b. p.)
Triethylene glycol carbonate $[-(CH_2CH_2O)_3COO-]_n$ probably mixture of monomer and dimer	47.7	6.8	(176)*n*	47.6	6.8	266 284 (b. p.)
Tetraethylene glycol carbonate *monomer* $[-(CH_2CH_2O)_4COO-]$	49.1	7.3	220	48.9	7.3	216 211
Decamethylene oxalate *monomer* $[-(CH_2)_{10}OCOCOO-]$	63.2	8.8	228	63.4	8.7	220 222
Undecamethylene oxalate *monomer* $[-(CH_2)_{11}OCOCOO-]$	64.5	9.1	242	64.4	9.1	253
Decamethylene malonate *monomer* $[-(CH_2)_{10}OCOCH_2COO-]$	64.5	9.1	242	64.5	9.1	238
Decamethylene succinate *dimer* $[-(CH_2)_{10}OCOCH_2CH_2COO-]_2$	65.6	9.4	512	65.4	9.3	478
Ethylene sebacate *monomer* $[-(CH_2)_2OCO(CH_2)_8COO-]$	63.1	8.9	228	63.1	8.9	
Ethylene sebacate *dimer* $[-(CH_2)_2OCO(CH_2)_8COO-]_2$	63.1	8.9	456	63.3	9.0	431 433 (b. p.)
Ethylene 1,11-undecanedioate *monomer* $[-(CH_2)_2OCO(CH_2)_9COO-]$	64.5	9.1	242	64.2	9.4	
Ethylene 1,11-undecanedioate *dimer* $[-(CH_2)_2OCO(CH_2)_9COO-]_2$	64.5	9.1	484	64.3	9.3	451 (b. p.)
Ethylene 1,12-dodecanedioate *dimer* $[-(CH_2)_2OCO(CH_2)_{10}COO-]_2$	65.6	9.4	512	65.6	9.4	481 (b. p.)
Ethylene brassylate *dimer* $[-(CH_2)_2OCO(CH_2)_{11}COO-]_2$	66.7	9.6	540	66.7	9.6	494 (b. p.)
Ethylene 1,14-tetradecanedioate *dimer* $[-(CH_2)_2OCO(CH_2)_{12}COO-]_2$	67.6	9.6	568	67.6	9.5	
Trimethylene sebacate *dimer* $[-(CH_2)_3OCO(CH_2)_8COO-]_2$	64.5	9.1	484	63.8	9.2	
Self-ester of ω-hydroxypentadecanoic acid *dimer* $[-(CH_2)_{14}COO-]_2$	75.0	11.7	480	75.0	11.8	

Small samples of monomeric decamethylene, dodecamethylene, tridecamethylene, and tetradecamethylene carbonates were heated for twenty hours at 200° together with parallel samples each containing a trace of potassium carbonate. The uncatalyzed samples of tridecamethylene and tetradecamethylene carbonates showed a considerable increase in viscosity; the decamethylene and dodecamethylene carbonates a much larger increase. The catalyzed samples of decamethylene and dodecamethylene carbonates were completely changed to solid, waxy polymers; while the catalyzed samples of the other two esters were still semi-solid.

Samples of dimeric hexamethylene and decamethylene carbonates, both with and without traces of potassium carbonate, were heated for eight hours at 200°. The catalyzed samples changed to very viscous liquids which solidified to hard waxes; the uncatalyzed samples were unchanged.

Summary

By heating linear polyesters with catalysts under certain conditions it is possible in many cases to bring about a smooth depolymerization to the corresponding monomeric and/or dimeric esters. This method makes it possible for the first time to prepare macrocyclic esters in good yields. Thirty new macrocyclic esters are described, mostly esters of dibasic acids. The cyclic carbonates and oxalates are obtained most easily. The ratio in which the two forms, monomer and dimer, are obtained is determined in part by the experimental conditions and in part by the nature of the ester—especially by its unit length. Monomers of 7 to 12 atoms are especially difficult to obtain.

WILMINGTON, DELAWARE
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Studies of Polymerization and Ring Formation. XXI. Physical Properties of Macrocyclic Esters and Anhydrides. New Types of Synthetic Musks

BY JULIAN W. HILL AND WALLACE H. CAROTHERS

Odors.—The monomeric cyclic anhydrides and cyclic esters described in the two preceding papers have highly characteristic odors. In particular some of the higher members have odors closely resembling musk. This observation is especially interesting because of the bearing of odor on the general problem of macrocyclic compounds.

The essential principles of musk and civet are the macrocyclic ketones I and II. Ruzicka's demonstration[1] of this fact was followed by the discovery[2] that the lactones III and IV are odorous principles of angelica oil and musk-seed oil. These materials are highly valued as perfume ingredients. In spite of the great difficulties involved in their synthesis, a

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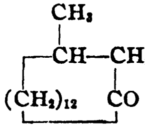
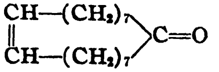
(1) Ruzicka, *Helv. Chim. Acta*, **9**, 230, 716, 1008 (1926).

(2) Kerschbaum, *Ber.*, **60**, 902 (1927); Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

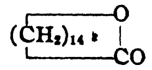
synthetic ketone ("Exaltone," cyclopentadecanone) and a lactone "Exaltolide") have been placed on the market as substitutes for the natural musks.



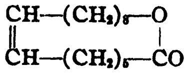
I



II



III

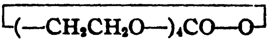


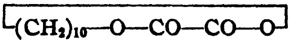
IV

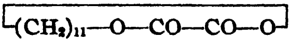
The observations on the anhydrides and carbonates are assembled in Table I, together with Ruzicka's data on the ketones and lactones. It will be noted that in each of the four series, with the possible exception of the ketones, odors are rather vague and indefinite until the number of atoms in the ring reaches 9. A camphoraceous or minty note then appears, and at about 13 atoms a woody or cedar-like quality. Beyond this point there is a nuance of musk which however in the anhydride series does not become definite and pronounced until the 15-atom compound is reached. At 15 or 16 atoms the musk quality approaches a maximum of fullness and homogeneity. Tetradecamethylene carbonate (17 atoms) shows a remarkable resemblance to "Exaltolide" (16-atom lactone). Beyond 18 or 19 atoms the odors in each series practically disappear.

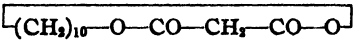
The structural feature common to the four series is the presence of one or more C=O groups as a member of a ring. It is rather extraordinary that the manner in which the C=O group is linked in the ring should make so little difference in the quality of the odor. On the other hand it appears that any modification of the C=O group itself completely changes the odor. Ruzicka, Schinz and Seidel report[3] that the alcohol corresponding to civetone has a faint and only slightly characteristic odor.

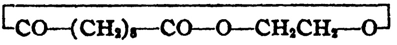
The fact that the only requirement (there are no doubt other limits not yet known) for musk-like odor is the presence of a C=O group in a ring of approximately 15 atoms is further illustrated by the following compounds not included in Table I (other physical properties of these compounds are listed in Table I of Paper XX)

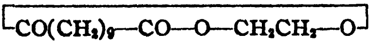

$(-CH_2CH_2O-)_4CO-O$ tetraethylene carbonate, 14 atoms, fresh, faint, musk-like


$(CH_2)_{10}-O-CO-CO-O$ decamethylene oxalate, 14 atoms, fresh, musk-like


$(CH_2)_{11}-O-CO-CO-O$ undecamethylene oxalate, 15 atoms, musk-like


$(CH_2)_{10}-O-CO-CH_2-CO-O$ decamethylene malonate, 15 atoms, faint, musk-like


$CO-(CH_2)_8-CO-O-CH_2CH_2-O$ ethylene sebacate, 14 atoms, musk-like


$CO(CH_2)_9-CO-O-CH_2CH_2-O$ ethylene undecanedioate, 15 atoms, musk-like

The first of these contains six oxygen atoms in the ring of which two are directly connected to the carbonyl group; the second and third have two

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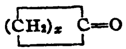
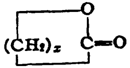
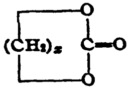
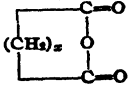
[3] Ruzicka, Schinz and Seidel, *Helv. Chim. Acta*, 10, 695 (1927).

TABLE I

ODORS OF CYCLIC COMPOUNDS

Atoms in ring	Ketones 	Lactones 	Carbonates 	Anhydrides 
5	Bitter almond and menthol	Fruity	Faint	Odorless
6	Bitter almond and menthol	Faint[a]	Faint	Odorless
7	Transition	Faint, spicy and floral[b]		Faint, pungent
8	Transition			
9	Camphoraceous		Minty, empyreumatic	
10	Camphoraceous		Minty, less empyreumatic	Spicy
11	Camphoraceous		Earthy, camphoraceous	Spicy
12	Camphoraceous		Earthy, camphoraceous	Spicy
13	Cedarwood, then musk		Cedar, faint rose and camphor	
14	Musk	Musk	Musk, camphoraceous	Aromatic
15	Pure musk	Musk and ambergris	Musk	Musk
16	Transition	Musk	Musk	
17	Civet	Civet	Musk	
18	Faint civet	Faint		
19	Faint			Musk
21			Faint	

[a] Observation on a specimen very carefully purified by F. J. Van Natta. [b] From unpublished work of F. J. Van Natta. This compound has not yet been described.

adjacent carbonyls to which annular oxygens are attached, in the fourth a methylene has been interposed between the two carbonyls, and in the fifth and sixth eight and nine methylenes are inserted between the carbonyls. It would be of great interest to have information on similar compounds in which the carbonyls are replaced by methylenes; unfortunately macrocyclic ethers are as yet entirely unknown.

From the practical standpoint the cyclic anhydrides are of no interest as odorous materials since they polymerize spontaneously on standing and the odors then disappear. (This fact incidentally demonstrates that the odors of the cyclic anhydrides are not due to any traces of the corresponding cyclic ketones which might conceivably be present as impurities.) On the other hand the cyclic esters, with the exception of the oxalates, are quite resistant to hydrolysis or polymerization and from the practical standpoint they have the advantage over the previously described ketones and lactones that they are formed in relatively high yields.

Molecular Refractions.—Ruzicka and Stoll have shown that the molecular refractions of macrocyclic lactones[4] and hydrocarbons[5] are lower by about 0.6 unit than the calculated values. The macrocyclic carbonates exhibit the same peculiar negative exaltation and to about the same degree. Typical data are assembled in Table II.

TABLE II

MOLECULAR REFRACTIONS OF CYCLIC ESTERS

Compound	Atoms in ring	M_D calcd.	M_D found	$E\ M_D$
Ethylene carbonate	5	17.15	16.87	−0.28
Trimethylene carbonate	6	21.77	21.92	+ .15
Octamethylene carbonate	11	44.86	44.45	− .41
Nonamethylene carbonate	12	49.48	49.05	− .43
Decamethylene carbonate	13	54.20	53.49	− .71
Undecamethylene carbonate	14	58.71	58.17	− .54
Dodecamethylene carbonate	15	63.33	62.66	− .67
Tridecamethylene carbonate	16	67.95	67.32	− .63
Tetradecamethylene carbonate	17	72.57	71.74	− .83
Octadecamethylene carbonate	21	91.04	91.05	+ .01
Tetraethylene glycol carbonate	14	49.79	50.21	+ .42
Decamethylene oxalate	14	58.72	59.12	+ .40
Undecamethylene oxalate	15	63.34	63.56	+ .22
Decamethylene malonate	15	63.34	63.63	+ .29

The last four compounds of the table appear to have a positive exaltation, but the amounts of these materials available were quite small and their purity was somewhat uncertain. The compounds for which negative values are listed were for the most part purified by crystallization. No significance can be attached to the fluctuations in these negative values

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(4) Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

(5) Ruzicka, Stoll, Huyser and Boekenoogen, *ibid.*, **13**, 1152 (1930).

from one member of the series to the next since the molecular refractions were not all taken at the same temperature.

Melting Points.—The melting points of the known macrocyclic compounds show little regularity in the nature of the change produced by increasing molecular weight but in the range of 8 to 14 atoms there is generally an oscillation from one member to the next.[5] The cyclic carbonates show a similar oscillation, the melting points and ring size for some of the monomeric polymethylene carbonates being

11	12	13	14	15	16	17
23°	35°	11°	41°	12°	25°	22°

Summary

Macrocyclic esters and anhydrides have odors closely resembling those of the ketones and lactones of the same ring size. The rings in the neighborhood of fifteen atoms have musk-like odors. The molecular refractions show a negative exaltation. Melting points in the carbonate series oscillate from one member to the next.

WILMINGTON, DELAWARE

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Studies of Polymerization and Ring Formation. XXII. Stereochemistry and Mechanism in the Formation and Stability of Large Rings

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

A great deal of discussion has been devoted to stereochemistry and mechanism in the formation of rings, but on account of the limited range of experimental facts available, fruitful discussion has been largely restricted to rings containing fewer than eight atoms. The only important series exemplifying closure of long chains hitherto has been the macrocyclic ketones which Ruzicka obtained by heating salts of the higher dibasic acids. As a basis for theoretical inferences this general reaction suffers from two disadvantages. The macrocyclic ketones are formed in such small yields (0.1 to 5%) that they can hardly be regarded as major reaction products, and the nature of the reaction (thermal destruction at high temperatures) is such that its mechanism is inherently obscure. Data on the polyesters and anhydrides now provide the possibility for a much clearer insight into the mechanism of the formation of large rings.

Following the demonstration of the stable existence of large carbon rings, Baeyer's theory of negative strain has been generally abandoned and replaced by the idea of Sachse and Mohr[1] that large rings may exist in

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(1) Mohr, *J. prakt. Chem.*, **98**, 348 (1918).

strainless and non-planar forms. A carbon chain constructed from conventional wire tetrahedra in such a way as to allow free rotation about each single bond clearly shows that the chain can assume a great multiplicity of shapes. If the number of atoms is five or six, the model is readily rotated so that the ends collide once in each complete rotation. If the number is more than six the ends can be brought together arbitrarily without any difficulty to produce a non-planar ring, which is quite flexible and can be bent into a variety of shapes without any appreciable strain. Considering the chain model as a representation of the bifunctional molecule, it is evident why rings of 5 and 6 atoms are readily formed and stable Larger rings should be equally stable, but it is obvious that their formation may present some difficulties. The chain can assume a great multiplicity of shapes; the particular configurations requisite for ring closure are relatively few. If then the molecule is placed under conditions where mutual reaction of its terminal groups can occur, the probability of *inter*molecular reaction is very much greater than that of *intra*molecular reaction. Hence, as has been demonstrated in previous papers of this series, reactions that might conceivably yield large rings from open chains almost invariably yield linear polymers instead. It is necessary again to emphasize this point since even some of the most recent writings on the subject of forming large rings still convey the impression that attempts to close long chains do not result in any clear-cut reaction at all. In fact, in most cases, reaction occurs perfectly smoothly without any difficulty but the reaction is intermolecular not intramolecular.

What means are available for controlling this situation? Obviously nothing much can be expected from any modification of the nature of the terminal groups. Even if these groups are of such a nature (*e. g.*, NH_2 and COOH) as to exercise a strong attraction for each other, this pre-existing attraction may itself be intermolecular rather than intramolecular.[2]

There is in fact no method known for controlling experimentally the shape that molecules assume. The possibility of such control may perhaps exist in the use of surface forces, but nothing is known about this matter. There are however two possible methods of controlling the result of the reaction. (1) High dilution will increase the *relative* probability of intramolecular reaction.[3] (2) If a series of mutually dependent and quantitatively reversible reactions is involved, constant removal of any traces of cyclic product will cause a displacement of the equilibrium with the ultimate conversion of the entire sample into the cyclic product. This is the principle involved in the synthesis of the cyclic esters and anhydrides described above.

In speculations devoted to Ruzicka's ketone synthesis it has been sug-

[2] The idea that such attractions may favor intramolecular reaction has been suggested by Mills, "Proceedings, Fourth International Solvay Conference," 1931, p. 20.

[3] *Cf.* Ruggli, *Ann.*, **392**, 92 (1912).

gested[2,4] that the peculiarity of the reaction which makes possible this very exceptional closure of large rings lies in the ability of the metal ion (*e. g.*, thorium) to bring the ends of the chain into a position of close intramolecular approach. But no reason is offered to explain why the metal ion should have such a peculiar effect; and the force of this suggestion is moreover considerably weakened by the claim[5] that macrocyclic ketones are obtained by thermal destruction not only from salts of dibasic acids but also from the acids themselves and their anhydrides. It appears to have been taken for granted in these speculations that reaction *is* intramolecular and leads directly to the cyclic ketone. This is a point that appears to be open to test and the following experiment was accordingly made.

Thermolysis of Thorium Octadecanedioate in Dixylylethane.—Twenty-five grams of thorium octadecanedioate, prepared by the method of Ruzicka, and 150 cc. of unsymmetrical dixylylethane were placed in a 300-cc. flask fitted with a stirrer and thermometer. The mixture was heated by means of a metal bath to 325°. In the course of ten minutes the suspended solid became gummy and attached itself to the stirrer. At the end of fifty minutes the mixture had become homogeneous but very viscous. At the end of two hours, heating was stopped. On cooling, the melt solidified to a slightly elastic gel. Some solid material (apparently unchanged salt) around the top of the flask was discarded. The gel was continuously extracted with ether for eighteen hours, whereupon it disintegrated to a light gray powder. It was further extracted for four hours with benzene, dried, heated with concentrated hydrochloric acid for three hours, separated, ground in a mortar, extracted for three hours with hot hydrochloric acid, then twice with hot alcohol and once with ether. The dried residue (10 g.) was an almost pure white powder. It was practically free of ash and melted at 126–128°; soluble in hot toluene, butyl alcohol and acetylene tetrachloride.

Anal. Found: C, 78.22, 78.89; H, 12.29, 12.41.

When triturated with aqueous sodium carbonate and thoroughly washed and dried it was converted to a salt (Na found, 1.16, 1.36%). The analytical data are consistent with the formula $HOOC[(CH_2)_{16}CO]_7OH$, the calculated values for C and H being 78.9 and 12.4% while a monosodium salt would contain 1.25% Na.

A sample of this material was placed in a molecular still and heated by a metal bath at 300–305°. At the end of one day a film of white solid distillate had collected on the condenser. It had a very pronounced fragrant musky odor.

Our interpretation of this experiment is that the thorium salt of the acid, as in other bifunctional reactions involving long chains, breaks down with the formation of a linear polymer

$$\ldots\text{—RCO—RCO—RCO—RCO—RCO—}\ldots$$

The resulting polyketone comprises the solid product remaining from the extraction. When the polyketone is heated in the molecular still, it cracks and appreciable amounts of the monomeric cyclic ketone (cycloheptadecanone) are produced; the characteristic musk-like odor therefore first makes its appearance at this point in the experiment.

The facts recited above place the macrocyclic ketones, esters (including

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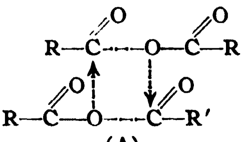
(4) Ruzicka, Stoll and Schinz, *Helv. Chim. Acta*, **11**, 670 (1928).

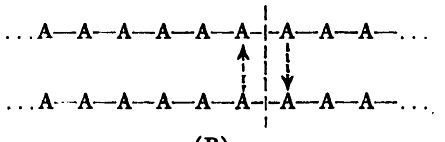
(5) Ruzicka, Brugger, Seidel and Schinz, *ibid.*, **11**, 496 (1928).

lactones) and anhydrides on a common basis for discussion so far as the stereochemistry and mechanism of formation are concerned.

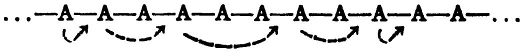
The α-polyanhydrides for example may be represented by the formula ...—CORCOO—CORCOO—CORCOO—CORCOO—.... They are apparently open chains, and contain no more than traces of cyclic anhydrides of low molecular weight. The possibility of converting the polymeric α-anhydrides into β-anhydrides of low molecular weight depends in the first place on the very great reactivity of carboxylic anhydrides and the fact that they are capable of reacting with themselves. A mixed anhydride such as that derived from acetic and butyric acids will, at least at elevated temperatures, pass into an equilibrium mixture containing a considerable proportion of the two simple anhydrides.[6] The process is analogous to ester interchange and, like that, doubtless proceeds through the formation of an addition product involving the ether oxygen of one molecule and the carbonyl carbon of another (A). A linear polyanhydride is not a chemical individual. It is a mixture of long chains of slightly differing lengths each of which bears a series of anhydride linkages. It presents a very complicated series of possibilities of reacting with itself. Adjacent chains can react with themselves to produce simultaneously longer and shorter chains (B). Reaction in a similar manner at two points will yield large rings and these may mutually coalesce by the same mechanism to produce still larger rings. Intramolecular reaction may result in the formation of cyclic monomers and dimers, etc.



(A)



(B)



The potentialities of the situation are sufficiently complex to suggest that at equilibrium the number of entities involved will be limited only by the magnitude of the sample. No doubt a condition of genuine equilibrium is impossible to achieve; nevertheless, experiment shows that at elevated temperatures quite a considerable series of transformations occurs, and it leads chiefly to the formation of very large molecules. At the same time appreciable amounts of smaller cyclic fragments (β-anhydride) are produced. The actual concentration of these β-anhydrides present in the reaction mixture at any time must be small, since the β-anhydrides polymerize almost instantly at the temperature involved; and their rate of formation cannot be exceedingly great because even at elevated temperatures where the speed and amplitude of molecular vibrations are greatly

(6) *Cf.* Autenrieth, *Ber.*, 34, 168 (1901).

increased, the relative probability of the configurations necessary for the formation of such cyclic compounds must be rather low. However, in the molecular still a mechanism is provided for removing and isolating the β-anhydrides as fast as they are produced. The equilibrium is thus continuously displaced and the entire specimen is finally converted into the β-anhydride.

A precisely similar mechanism is unquestionably involved in the formation of macrocyclic esters from polyesters and it is significant in this connection that smooth transformation requires the presence of ester-interchange catalysts.

The ketones obviously present a more difficult case. No mechanism corresponding to ester interchange exists for the smooth rupture of the linkages joining the structural units in a chain of the type ...—CO—R—CO—R—CO—R—...; nor would one expect a macrocyclic ketone to polymerize with the formation of the corresponding polyketone. Since the reactions involved are not strictly reversible and there are many side reactions, the formation of cyclic ketones offers scarcely any possibilities for rational and deliberate control. The yields are therefore generally only a small fraction of those obtained with the cyclic carbonates, oxalates and anhydrides.

Steric Interferences.—The outline presented above is incomplete since the possible influence of atoms attached to the carbon chain has been ignored. Such atoms are capable of acting as obstacles to ring closure, and they may also introduce strains into rings. For the series under consideration hydrogen is the most numerous and important peripheral atom. The internuclear C–H distance is known from spectroscopic data to be 1.08 Å., and since the (aliphatic) carbon radius is 0.77 Å., the distance from the center of the hydrogen to the surface of the carbon is 0.31 Å. This indicates an atomic diameter of 0.62 Å. for hydrogen attached to carbon. But hydrogens not mutually joined will be expected to exercise a mutual repulsion preventing close approach, and data on the densities of hydrocarbons, collision areas, etc., show that the average distance between the centers of hydrogens belonging to separate molecules is always greater than 0.62 Å. The combined hydrogen atom must therefore be assigned, in addition to its internal radius of 0.31 Å., a larger external radius, which defines the closest average approach of other atoms.[7] This external radius will vary with the compound and the conditions; it will decrease with increasing temperatures and will be larger in a crystal than a gas. The most elaborate experiments and speculations on the external radius of hydrogen are those of Mack,[8] who in different cases uses values ranging from 0.49 to 1.26 Å. Stoll and Stoll-Comte[9] had, however, already made specific

(7) *Cf.* the excellent review by Sidgwick in "Annual Reports of the Progress of Chemistry for 1932."

(8) Melaven and Mack, THIS JOURNAL, **54**, 888 (1932); Sperry and Mack, *ibid.*, 904; Mack, *ibid.*, 2141.

(9) Stoll and Stoll-Comte, *Helv. Chim. Acta*, **13**, 1185 (1930).

application of the external domain of hydrogen atoms in connection with macrocyclic hydrocarbons. They pointed out that the cyclic paraffins exhibit two anomalies. (1) When density is plotted against number of CH_2 groups a maximum appears in the range of 10 to 17 atoms, and (2) it is within this range that the yields of the cyclic ketones fall to an exceedingly low minimum. The explanation which they offer is very briefly this. Consideration of the densities of cyclic and open-chain hydrocarbons indicates a domain for the CH_2 group that can be accounted for by representing the hydrogen as spheres of diameter 2.3 Å. (compared with 1.54 Å. for carbon). Rings of 5, 6 or 7 members therefore consist of an approximately flat cyclic chain of carbon atoms with a shell of much larger hydrogen atoms around the periphery. In rings of 8 to 15 atoms the geometrical limitations imposed by the valence angles of the carbon atoms force some of the hydrogens toward the center of the ring. The space available is not sufficient to receive them; the "domain" of the hydrogens (or of the CH_2 group) is therefore reduced or compressed. The resulting strain explains the minimum in the yield of the cyclic ketones, and the compression explains the maximum in the density curve of the hydrocarbons. The turning in of hydrogens toward the center of the ring is illustrated for cyclononane by Fig. 1 in which the diameter of the hydrogens (1.18 Å.) is much smaller than that assumed by Stoll and Stoll-Comte (2.3 Å.). This configuration is quite rigid and it is evident that if the hydrogens were twice as large, the space available would not be adequate to receive them. As the size of the ring increases the number of hydrogens forced toward the center increases; above 15 atoms half of them are forced toward the inside of the ring, but there is sufficient space to accommodate them and no strains are developed.

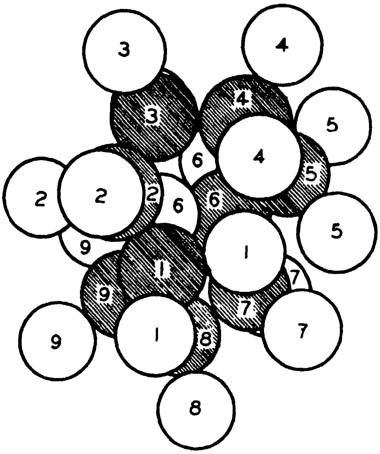


Fig 1.—Cyclononane (carbon, d = 1.54; hydrogen, 1.1). This model illustrates the cramped nature of the ring and the turning of hydrogen toward the center.

This idea of steric interferences due to "external" radii is capable of many interesting applications to the cyclic esters and anhydrides. It is unfortunately for this purpose impossible to assign any exact value to the external radius of hydrogen. Results obtained in the diphenyl problem[10] suggest that the value implied in a spherical hydrogen of 2.3 Å. is probably much too large; however, for immediate qualitative purposes the exact value adopted is not particularly important. The following discussion is based on observation of models in which the hydrogen is represented as a sphere of radius 2.2 Å.

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[10] *Cf.* Adams and Yuan, *Chem. Reviews*, **12**, 261 (1933).

When a zig-zag hydrocarbon chain is constructed with such large hydrogens, it is immediately evident that the mobility of the chain is greatly reduced. The hydrogens interfere with many rotational movements that would present no difficulty if the hydrogens were absent. The interferences toward ring closure become exaggerated as the length of the chain is increased beyond 6 or 7 atoms. For a cycloparaffin of 9 atoms the interferences are so serious that the model is not constructible.

If an oxygen atom is inserted in the chain, the flexibility of the model is considerably increased, since this insertion is practically equivalent to the removal of two of the interfering hydrogens.[11] Actually also oxygen probably presents less resistance to the deflection of its valence angles, although this is not illustrated by the models. In the anhydrides and esters under consideration each structural unit contains in its chain at least one oxygen and at least one carbonyl carbon (which also bears no hydrogens). The result is a great increase in the constructibility of the models. Construction of models of the cyclic hydrocarbons in the range of 9 to 15 atoms requires either a compression of the hydrogen spheres or a considerable deflection of the angles. In the carbonates and anhydrides the entire series of monomers from the 5-atom ring up can be constructed from spherical wooden atoms without more than very slight deflection of the angles. From this one may infer that no maximum should appear in the curve relating density to ring-size of the carbonates. The experimental curve is shown in Fig. 2. Unfortunately data are lacking in the range of 7 to 10 atoms, but the nature of the curve makes it very improbable that any maximum exists.

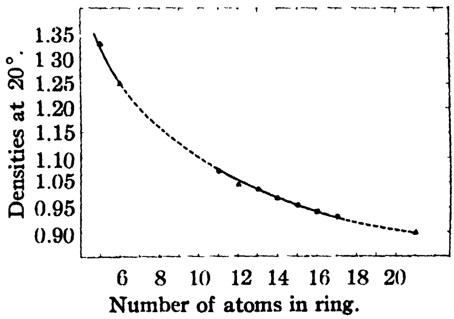

Fig. 2.—Densities of monomeric cyclic polymethylene carbonates at 20°: ⊙, values determined at 20°; ⊡, values obtained by extrapolation via molecular refractions from determinations of density made at 25°; △, values obtained by extrapolation via molecular refractions from determinations made at 50°.

Although it appears from the models that no compression of the hydrogen domains is involved in any of the cyclic ester or anhydride molecules, the manipulation of the models shows that there is a great difference in ease of ring closure depending upon the length of the chain. In the range of 8 to 14 atoms the interferences are so numerous that many trials and errors must occur before the particular configuration that permits ring closure is found; and the ring when closed is then very rigid. In the carbonate series with the 15-membered ring the model acquires considerable flexibility.

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[11] This effect is probably considerably exaggerated in the models since the oxygens are represented only by their internal diameters.

The greater ease in constructibility of rings of 15 atoms or more explains why in the preparation of carbonates in the range of 7 to 12 atoms the products are almost exclusively the dimeric forms. At equilibrium the concentration of dimer will be large compared with the concentration of monomer. But as the ring size increases not only does the ease of monomer formation approach (and ultimately exceed) that of the dimer, but the latter becomes relatively more and more difficult to remove by evaporation. The ring-size at which the two forms begin to appear in equal amounts will depend partly upon the experimental conditions; but it will also be controlled to a certain extent by the nature of the ring. It is interesting in this connection to compare the three 14-membered rings undecamethylene carbonate, tetraethylene glycol carbonate and decamethylene oxalate. The first has two annular oxygens and one carbonyl, the second two oxygens and two carbonyls and the third five oxygens and one carbonyl. The first compound under the conditions used gave a mixture of monomer and dimer, the last two gave exclusively monomer.

The alkylene esters of dibasic acids above malonic yield chiefly dimers even when the unit length is as great as 18. The models do not furnish any very clear explanation of this fact although it appears that some advantage in ease of ring formation may be expected if the oxygens and carbonyls are all adjacent (as in oxalic esters).

The cyclic anhydrides present the same reluctance toward the formation of rings of intermediate size as do the esters, but they show some peculiarities. The products appear to be invariably either monomer or dimer, not mixtures of the two. The range of dimer formation is from 9 to 13 atoms (unit length). Very peculiar is the fact that the two even membered compounds (10 and 12 atoms) in this range appear to yield exceedingly unstable monomers rather than dimers. The result is the alternating effect shown graphically in Table I (p. 5025). The manipulation of models in this range furnished the impression that even-membered rings were more readily constructed than odd, but the geometrical peculiarity responsible for this effect was not identified. All of the cyclic anhydrides are exceedingly unstable at the high temperatures used in their formation, and the nature of the β-anhydrides produced might therefore be expected to be very sensitive to very slight differences in the ease of constructibility.

Ring Stability.—Ruzicka showed[12] that his macrocylic paraffins were not destroyed by the action of phosphorus and hydriodic acid at 250° and his cyclic ketones resisted the action of fuming hydrochloric acid at 180–

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[12] Ruzicka, Brugger, Pfeiffer, Schinz and Stoll, *Helv. Chim. Acta*, **9**, 499 (1926).

190°. This was an indication that large rings are no less stable than those of 5 or 6 atoms and a refutation of the idea that large rings are strained. It appears, however, in view of the results obtained with the cylic esters and anhydrides, that this conclusion requires some revision. The higher cyclic anhydrides all polymerize very readily. In this respect the large rings are very unstable as compared with those of 5 to 6 atoms, which do not polymerize at all. The instability rises to a maximum with the rings of 10 to 12 atoms, which polymerize rapidly even at temperatures below 0°. At elevated temperatures (*e. g.*, 200°) the macrocyclic esters also polymerize. It is therefore very difficult to accept the conclusion that large rings are entirely free from strain. Our interpretation of the facts is as follows.

Rings of 3 or 4 atoms have very large strains owing to the necessarily large deflection of the annular valences. Rings of 5 atoms are practically free of strain. Most rings of 6 atoms are strained. It is true that cyclohexane can be represented as existing in two strainless forms (*cis* and *trans*) but since it has not been possible to isolate two cyclohexanes, it seems likely that the two forms are in dynamic equilibrium. On each conversion of one form into the other the ring must pass through a nearly planar position of strain. The existence of such strain is indicated by the fact that all simple 6-membered cyclic esters polymerize very readily. (Glutaric anhydride does not polymerize but the oxygen valences in this case may permit sufficient deflection to avoid strain.) Larger rings are all strained. In the range of 7 to 14 atoms where the models are very rigid the strain may be pictured as due to the mutual repulsion of non-linked peripheral atoms that are crowded against one another. In larger, more flexible rings the vibrations due to thermal agitation constantly present the possibility of introducing momentary strains. This effect is similar to that pictured for the cyclohexane ring but is probably less pronounced. At any rate, 6-membered cyclic esters polymerize more readily than macrocyclic esters.

The ease of polymerization of the macrocyclic anhydrides is unquestionably associated with the extraordinary reactivity of anhydrides generally. A facile mechanism for the rupture of the ring is provided by the nature of the anhydride linkage and hence very slight strains or distortions, which may arise merely through small interferences among substituent atoms, need not be tolerated. The macrocyclic esters polymerize by a similar mechanism (*i. e.*, by ester interchange) but less readily because they are less reactive. The apparent high stability of the macrocyclic hydrocarbons and ketones is due to the fact that they present no point of easy chemical attack; if a sufficiently delicate chemical probe were available they would probably prove to be somewhat less stable than those of 5 atoms.

Summary

It is shown that the formation of macrocyclic ketones from salts of the dibasic acids probably involves first a linear polyketone which is subsequently cracked or decomposed. The ketones thus follow a course already established for esters and anhydrides. The characteristic analogies and differences in the three series can be explained by taking into account the nature of the reactions involved and the steric effects of peripheral atoms. Rings of more than 5 atoms cannot be regarded as entirely strainless. The probable nature of the strains in large rings is indicated.

WILMINGTON, DELAWARE RECEIVED SEPTEMBER 2, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride. VI. The Reaction of Acetamide with Alcohols and Phenol

BY FRANK J. SOWA AND JULIUS A. NIEUWLAND

The purpose of this paper is to describe the formation of esters by the removal of ammonia, in the form of monoammino boron fluoride,[1] from the acetamide–boron fluoride compound[2] and a second compound of the type ROH. The reaction takes place according to the equation

$$CH_3CONH_2{\cdot}BF_3 + ROH \text{ — } CH_3CO_2R + BF_3{\cdot}NH_3$$

By this method the acetates of methyl, ethyl, isopropyl, *n*-butyl and *tert*-butyl alcohols and of phenol have been prepared in yields of 71, 69, 32, 50, 38 and 50%, respectively. The percentage yield depends upon the amount of boron fluoride used (as long as the latter is not in excess). This seems to indicate that the formation of the monoammino boron fluoride is the driving force of the reaction. From the foregoing results it is predicted that the acetamide–boron fluoride compound should be a good acetylating agent.

Various amides and alcohols are being studied in connection with this reaction. The reaction of the acetamide–boron fluoride compound with amines, acids, esters and hydrocarbons is also being examined.

Experimental

One mole of the alcohol or phenol was introduced into a 500-cc. flask containing the acetamide–boron fluoride compound, prepared by passing a mole of boron fluoride into a mole of acetamide. In a few cases monoammino boron fluoride separated as a white solid almost immediately. The flask was fitted with a reflux condenser and the mixture was refluxed

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(1) Kraus and Brown, THIS JOURNAL, 51, 2690 (1929); Mixter, *Am. Chem. J.*, 2, 153 (1881); Pflaum and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, 4, 392 (1932).

(2) Bowlus and Nieuwland, THIS JOURNAL, 53, 3835 (1931).

from fifteen to forty-five minutes. The ester was then distilled directly from the flask through a fractionating column.

The solid residue, after organic matter had been removed, was shown by analysis to contain one mole of ammonia. When treated with concentrated sulfuric acid and heated, the residue gave a large amount of boron fluoride gas. It is possible to recover practically all of the boron fluoride by the treatment with sulfuric acid.

Summary

It has been shown that the addition compound formed between acetamide and boron fluoride reacts rapidly with alcohols and with phenol to form acetates and monoammino boron fluoride.

NOTRE DAME, INDIANA RECEIVED OCTOBER 4, 1933
PUBLISHED DECEMBER 14, 1933

Notes

Note on the Oxidation Products of Benzophenone Oxime[1]

BY W. H. HUNTER AND W. S. DYER

The work presented in this paper was begun a number of years ago, but unfortunately it had to be interrupted before it was completed. Recently, v. Auwers and Wunderling[2] have published a paper under the above title, and it therefore seems advisable for us to present a summary of our own work in this field, even though it is still incomplete.

Oxidation with Ferricyanide.[3]—Twenty grams of benzophenone oxime was dissolved in 200 cc. of ethyl alcohol by adding a small amount of 1:1 aqueous sodium hydroxide. This solution was then added to one liter of ice cold alkaline ferricyanide (40 g. of ferricyanide, 40 g. total of sodium hydroxide). The temperature was kept at 0° and the mixture stirred for two hours. The floating blue mass was removed and boiled with 500 cc. of ethyl alcohol, filtered from the fine white precipitate, and the alcohol evaporated. The residue was stirred repeatedly with separate portions of petroleum ether, and was again boiled with ethyl alcohol and filtered. Several such alternations of solvents gave three products: (I) a compound soluble in alcohol and in petroleum ether; when "seeded" with benzophenone it gave crystals melting at 47°. When mixed with benzophenone the melting point was unchanged; yield, 11 g. (II) a compound soluble in alcohol and insoluble in petroleum ether. Recrystallized from hot alcohol, this gave 2 g. of yellow needles, m. p. 156–157°.

Anal. Calcd. for $C_{26}H_{20}ON_2$: C, 82.98; H, 5.32; N, 7.45; mol. wt., 348. Found: C, 82.98; H, 6.1; N, 7.51; mol. wt. by freezing point in benzene, 357.

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(1) Part of the work presented in this paper is taken from a thesis by Walter S. Dyer presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Master of Science, September, 1925.—L. I. SMITH.

(2) v. Auwers and Wunderling, *Ber.*, **66**, 538 (1933).

(3) Holleman, *Rec. trav. chim.*, **13**, 429 (1894).

(III) a compound insoluble in alcohol. This was boiled with fresh portions of alcohol until the constant m. p. 193° with decomposition was reached; yield, 4 g., white powder.

Anal. Calcd. for $(C_{13}H_{10}NO)_4$: C, 79.53; H, 5.14; N, 7.1; mol. wt., 728. Found: C, 79.63; H, 5.08; N, 7.06; mol. wt. by freezing point in benzophenone, 722.

That the product (II) retains the benzophenone nucleus seems certain since (1) with boiling 3 *N* hydrochloric acid an 87% yield of benzophenone results; (2) with boiling concentrated hydrochloric acid almost 100% conversion to benzophenone occurs; (3) attempts at reduction yield benzophenone.

That the product (III) retains the benzophenone nucleus seems certain since, (1) upon reduction, benzophenone and benzophenone oxime are produced; (2) with phosphorus pentachloride in dry ether benzophenone and benzanilide are formed; (3) with glacial acetic acid benzophenone is obtained; (4) with boiling acetone the compound slowly decomposes to benzophenone and benzophenone oxime; (5) after standing for a year small amounts of benzophenone can be extracted with alcohol.

Oxidation with Iodine in a Dry Medium. Preparation.—The sodium salt of the oxime was prepared by adding a solution of 0.5 g. of sodium in 10 cc. of absolute alcohol to 4.3 g. of benzophenone oxime dissolved in 25 cc. of dry ether. The mixture was placed in a vacuum until only a sirupy mass remained. 100 cc. of dry ether was added and the mass stirred for several minutes until a white precipitate appeared. The container and contents were placed in a desiccator for several hours and then filtered rapidly. The white solid was washed with dry ether and dried in a vacuum.

(1) Iodine and the dry sodium salt of benzophenone oxime were placed in separate containers in a vacuum. The iodine vaporized and the sodium compound became dark brown and wax-like. This brown waxy material was moistened with water and a bright greenish-blue color appeared which soon changed to yellow. The products were benzophenone, a red tar-like mass, and a 65% yield of sodium iodide.

(2) 4.5 grams of the dry sodium salt was placed in 100 cc. of dry benzene. To this was slowly added, with shaking, 2.6 g. of iodine in 100 cc. of dry benzene. Rapid decolorization took place until about one-half the iodine had been added. The mixture was put on the shaker for twelve hours and then filtered. The filtrate was distilled under reduced pressure. The residue from the distillation yielded 2 g. of benzophenone and 1.25 g. of a tarry mass which contained iodine, as well as sodium iodide, sodium salt of the oxime, and oxime. Similar results were obtained by boiling under reflux for one-half hour instead of shaking, or by using pyridine as the solvent.

Oxidation with Silver Oxide. (1) In Benzene.—Five grams of benzophenone oxime was dissolved in 100 cc. of dry benzene. To this was added 5.8 g. of freshly precipitated and dried silver oxide, together with a little anhydrous sodium sulfate, and the mixture was boiled under reflux for two hours. By this time a silver mirror had formed on the flask, and the solution was deep yellow. The mixture was filtered and the benzene distilled. The residue from the distillation was stirred with petroleum ether until it solidified. The solution contained 1.3 g. of benzophenone. The residue was boiled with alcohol and gave 0.1 g. of compound (III). The alcohol solution contained a mixture which could not be separated.

(2) In Ether.—Twenty-five grams of benzophenone oxime was dissolved in 200 cc. of dry ether and to this was added 42 g. of silver oxide. The mixture was boiled under reflux for eighteen hours, filtered, and the ether evaporated. The residue from the evaporation when subjected to alternate alcohol and petroleum ether treatments gave a yield of 17 g. of benzophenone and 3 g. of compound (I).

Summary.—Benzophenone oxime has been oxidized in aqueous and non-aqueous media. The definite products are benzophenone, a yellow

compound $C_{26}H_{20}ON_2$, melting at 156–7°, and a white compound $(C_{13}H_{10}NO)_4$, melting at 193° with decomposition.

SCHOOL OF CHEMISTRY
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RECEIVED JUNE 30, 1933
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An Improved Method of Preparing Diethylgermanium Derivatives

BY L. HORVITZ AND E. A. FLOOD

In a previous paper[1] a method of preparing diethylgermanium derivatives, involving bromination of triethylgermanium fluoride, was described. A much simpler and more economical method of preparing these compounds is as follows.

Ethylgermanium triiodide and an excess of 40–60 lead–bismuth alloy are heated together, in the absence of air, to 150° for one or two days, shaking occasionally to subdivide the molten metal into droplets. When reaction appears complete the product is extracted with dry ether or ligroin, preferably in the absence of air. After distilling off the solvent the viscous yellow residue[2] is dissolved in ethyl iodide and the solution, in an air-free sealed tube, heated at 125° for two or three days. The excess ethyl iodide is now distilled off and the impure diethylgermanium diiodide is purified by fractional distillation *in vacuo*. If the oxide is desired, the impure diiodide may be hydrolyzed with aqueous sodium hydroxide, boiled for a few minutes, cooled, and the diethylgermanium oxide filtered off.

The characteristics of these new substances are as follows: diethylgermanium dichloride ($(C_2H_5)_2GeCl_2$); colorless liquid with pungent odor; b. p. 175° (758 mm.); m. p. −39 to −37°; Ge, calcd.: 36.01%; found: 36.03, 35.76%; Cl, calcd.: 35.18%; found: 35.26, 35.17%. Diethylgermanium diiodide ($(C_2H_5)_2GeI_2$); colorless liquid; b. p. 252° (759 mm.); m. p. −2 to −1°; Ge, calcd.: 18.88%; found: 18.90, 18.85%; I, calcd.: 66.02%; found: 66.45, 66.27%.

When the former method of preparation is used considerable difficulty is encountered in separating the diethylgermanium derivatives from the triethylgermanium compounds usually present, whereas in the present method the probable impurities are monoethylgermanium derivatives which, being water-soluble, are easily removed. Where a supply of germanous sulfide is available the simplicity of the present method is particularly marked in that only four steps are involved all of which may be carried out in good yields while some eight steps were involved in the former method.

CHEMISTRY DEPARTMENT
BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

RECEIVED JULY 13, 1933
PUBLISHED DECEMBER 14, 1933

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[1] Flood, THIS JOURNAL, 54, 1667 (1932).

[2] Analyses of this residue indicated it to be impure $(C_2H_5GeI)_x$. Calcd.: I, 55.6%. Found: I, 58.5%. This interesting compound will be studied later.

The Octanes

BY FRANK C. WHITMORE AND K. C. LAUGHLIN

It is of interest to note that all eighteen of the structurally isomeric octanes have now been synthesized. This was accomplished when the three remaining trimethylpentanes were prepared by us [THIS JOURNAL, **55**, 2608 (1933)], although we were not aware at the time that we had completed the octane series. The preparation of the other isomers may be found as follows: Tafel and Jürgens, *Ber.*, **42**, 2548 (1909); Richard, *Ann. chim. phys.*, (8) **21**, 323 (1910); Noller, THIS JOURNAL, **51**, 594 (1929); Edgar and Calingaert, *ibid.*, **51**, 1546 (1929); Whitmore, Stehman and Herndon, *ibid.*, **55**, 3807 (1933); Parks and Huffman, *Ind. Eng. Chem.*, **23**, 1138 (1931); de Graef, *Bull. soc. chim. Belg.*, **40**, 315 (1931). Optical isomers of 3-methylheptane and 2,4-dimethylhexane have also been prepared [Levene and Marker, *J. Biol. Chem.*, **91**, 405, 761 (1931)].

PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

RECEIVED SEPTEMBER 29, 1933
PUBLISHED DECEMBER 14, 1933

COMMUNICATIONS TO THE EDITOR

THE MUTAROTATION OF α-*d*-GLUCOSE IN HEAVY WATER

Sir:

It is generally accepted today that mutarotation in reducing sugars and sugar derivatives of various types depends on the presence of a displaceable hydrogen atom. A rearrangement of bonds consequent upon the displacement of this particular hydrogen atom, as in the keto-enolic isomeric changes, causes the reversible conversion of an oxide sugar into the intermediate aldehyde. Hudson [*Z. physik. Chem.*, **44**, 487 (1903)] has shown that the equal velocities of mutarotation of the α- and β-forms of sugars are due to opposite parts of one balanced reaction, and [Hudson and Dale, THIS JOURNAL, **39**, 320 (1917)] that the velocity coefficients for α- and β-glucose, determined at eight temperatures from 0.7 to 40°, are identical. Since the mutarotation of the sugars is evidently due to the wandering of a mobile hydrogen atom, it was thought interesting to investigate the effect produced by the wandering of a heavy hydrogen atom in a sugar molecule. The following experiment was carried out at 18°. A sample of 1.0024 g. of α-*d*-glucose was dissolved in 5 cc. of distilled water, and the change of the rotation was measured in a 2-dm. semi-micro tube with sodium light. The first reading was taken six minutes after the addition of water. The velocity-coefficient was found to be $k_1 + k_2 =$

0.00546. The experiment was duplicated with heavy water of d_4^{20} 1.06. The velocity coefficient was found to be $k_1^1 + k_2^1 = 0.00290$. From these results it can be concluded (1) that on solution in heavy water of a reducing sugar the displaceable hydrogen atom of that sugar is *immediately* replaced by a heavy hydrogen atom of the heavy water, and (2) that the mutarotation is indeed due to oxo-cyclo desmotropy, *i. e.*, to a change in which the double bond of a $>C{=}O$ group is replaced by a ring formed by the migration of a hydrogen atom. The corresponding experiments with 100% heavy water will be carried out shortly.

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EUGENE PACSU

RECEIVED NOVEMBER 21, 1933 PUBLISHED DECEMBER 14, 1933

THE DEUTEROAMMONIAS

Sir:

Three different samples of heavy water have been brought to reaction in the vapor phase with magnesium nitride to form ammonias in which the hydrogen atoms are predominantly of mass 2. The densities of the three products, relative to that of ordinary ammonia measured under the same conditions, were, respectively, 1.12, 1.158 and 1.174. Assuming equal equations of state for all the ammonias, these densities correspond to ammonias containing, respectively, 68, 90 and 99% of heavy hydrogen. The gases have the odor of ammonia. The physical properties show a progressive change with isotope concentration as is seen from the following data:

Percentage of heavy hydrogen	0	68	90	99
Freezing point, °Abs.	195.2	197.9	198.6	199
Boiling point, °Abs.	239.75	241.7	242.1	242.3

By means of a differential tensimeter using ammonia as reference the following vapor pressures were obtained for the 99% product:

T, °Abs.	202.3	213	226.1	232.1	238.6
p_{NH_3}	77	184	364	511	714
p_{ND_3}	63	154	313	445	628

Assuming the latent heat of vaporization of ammonia to be 5797 cal. per mole at 1 atmosphere, the vapor pressure curve of the product gives a value for the latent heat of vaporization of ND_3 of 5990 calories per mole.

With the assistance of Dr. G. I. Lavin we have examined the absorption spectra of the products in the far ultraviolet and found them to be similar to, but quite distinct from, that of ammonia, well defined spectrograms having been obtained. Densitometer curves made from our plates by Dr. Garman of New York University show that the principal bands are placed further in the ultraviolet than are the corresponding bands of ammonia and have some structure on the short wave length side which is absent in corresponding ammonia bands. At longer wave lengths there are band systems not evident in the ammonia spectrum under similar operating conditions. The 68% product showed a larger number of these longer wave length absorption bands. It is possible that they may be associated with the presence in such preparations of the unsymmetrical molecule NHD_2. We are continuing these studies of absorption spectra and are extending them to the infra-red region. We are also extending the work in order to produce pure preparations of the mixed ammonias, the mono-deuteroammonia, NH_2D and the di-deuteroammonia, ND_2H. The chemistry of our products is also under study.

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HUGH S. TAYLOR
JOSEPH C. JUNGERS

RECEIVED NOVEMBER 22, 1933 PUBLISHED DECEMBER 14, 1933

ELECTROLYTIC SEPARATION OF HYDROGEN ISOTOPES AND THE MECHANISM OF THE CATHODE PROCESS

Sir:

Water containing approximately 7% deuterium was electrolyzed at 26° using platinum anodes and six different metals as cathodes, the electrolyte being potassium hydroxide initially 0.5 *N*. In addition, 0.5 *N* sulfuric acid was electrolyzed with cathodes of platinum and copper. The cathodic current density was 1 ampere per sq. cm. apparent area, but the surfaces were roughened with fine sandpaper. The extent of separation was determined by burning the hydrogen–oxygen mixture at a fine jet in a closed vertical Liebig condenser, collecting the water and measuring its density. All danger of explosion was avoided by inserting in the gas stream just above the jet a 10-cc. bulb filled with fine sand.

The ratio α of the specific rates of discharge is defined by the relationship $d \ln n_H = \alpha \, d \ln n_D$ where n_H and n_D are, respectively, the number of hydrogen and deuterium atoms in the electrolyte. The values obtained for α in the potassium hydroxide solution were: Pb 7.4, 7.2; Fe 7.6, 6.9; Pt 7.6, 6.5; Cu 6.8; Ni 5.5; Ag 5.3, 5.0. In the acid solution the values were: Pt 5.7, 5.7; Cu 5.5, 5.8.

The relation first given by Tafel connecting current and overvoltage has been interpreted by Volmer as showing that the slow process is the passage of a hydrogen ion over a potential barrier at the electrode surface, and Polanyi has suggested that this barrier is responsible for the isotope separation. The relative rates of discharge of the proton and deuton will depend upon two factors associated with the height and shape of the barrier, namely, the rates of leakage through the barrier, and the difference between the rates of activation arising from the different zero-point energies of the bonds H—O and D—O in the hydrated ions.

Bowden and Rideal's measurement of the capacity of the Helmholtz double layer at the surface of mercury and other metals indicates a separation of about 1.5 Å. between the oxonium ions in the electrolyte and the negative charge on the cathode. This width of barrier together with a reasonable estimate of its height and shape indicates that leakage through the barrier is of secondary importance. On the other hand, the zero-point energy difference between a hydroxyl and a deuteroxyl radical would make α equal to 12; of course the actual force constant will not be the same in the ions as in the radicals, but the observed figures of about 6 are not inconsistent with the view that the separation is almost entirely due to the zero-point energy difference.

If the slow process at the cathode were the combination of atoms to molecules on the surface, there would again be a separation due to the zero-point energy, but the *maximum* values calculated for α on this supposition are only about one-half the experimental values. Thus quite apart from arguments based on the magnitude of the constant in Tafel's overvoltage equation, it is clear that the slow process is not the combination of atoms, at any rate for these metals.

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H. EYRING

RECEIVED NOVEMBER 22, 1933 PUBLISHED DECEMBER 14, 1933

FURTHER EXPERIMENTS ON THE PHYSIOLOGICAL EFFECT OF HEAVY WATER AND OF ICE WATER

Sir:

A previous communication [THIS JOURNAL, 55, 4332 (1933)] reported greater longevity and less cell-disjunction in masses of *Spirogyra* in slightly concentrated deuterium oxide water of density 1.000061, which is in contrast to the lethal action of nearly pure H^2H^2O [*cf.* Lewis, *ibid.*, 55, 3503 (1933); Taylor, Swingle, Eyring and Frost, *J. Chem. Phys.*, 1, 751 (1933)]. The present report deals with short lengths of a filament of *Spirogyra nitida* in 5-cc. water samples exposed to northern light (temp. 10–14°). A representative filament of 31 cells in the isotope water had 43 cells after six days, of which 3 were dead; a filament of 37 cells in ordinary water showed no cell division at the end of six days and 20 cells died; in ice water renewed twice daily a filament of 50 cells showed 15 abnormal at the end of five days, while the filament in freshly condensed water renewed twice daily showed all of its 50 cells dead or shrunken in the same interval; the control filament (pond water) of this series had 47 cells initially and 64 normal cells after six days.

Oscillatoria spread more extensively in isotope water, possibly due to the *P*H of 6.77 (kindly determined by Dr. T. L. Jahn with a glass electrode) for the difference was not as great in water samples buffered to 7.12.

The heavy water effects may be due to its influence on enzyme for a sample of pancreatic amylase in solution in the deuterium water for twenty-four hours was not as active in digesting starch as a similar portion in ordinary water (the erythrodextrin stage was reached in eight minutes in isotope water and in six minutes in controls). In this case it is suggested that the hydrolysis is retarded by the deuterium apart from a *P*H effect. Also, in fermentation tests a decrease of 10% in carbon dioxide production was observed when zymase was exposed for sixty-six hours to the isotope water.

Ice water may also condition enzyme action for Nord and Weiss [*Z. physik. Chem.*, **166**, 1 (1933)] report increased activity of enzyme solutions which have been frozen, possibly due to disaggregation of enzyme particles. Experiments by one of us (E. J. L.) in the Biology Department of Clark University show that oxidation of guaiaconic acid by the peroxidase–oxygenase system is increased if the solution is made up in freshly melted ice water and allowed to come to room temperature. When a solution of guaiaconic acid and peroxidase, without an oxygenase or peroxide, is frozen, oxidation occurs when the ice melts.

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T. CUNLIFFE BARNES
E. J. LARSON

RECEIVED NOVEMBER 23, 1933 PUBLISHED DECEMBER 14, 1933

THE ISOTOPIC ANALYSIS OF WATER

Sir:

The spectral method which was used in the original discovery of deuterium is not capable of high precision. The oxides of the two hydrogens, however, have considerably different physical properties which afford a basis for precise analytical methods. Densities have been used extensively,[1] and we have found that the determination of the index of refraction by means of a Zeiss interferometer is simple, rapid, and very precise. We feel that our present experience with this instrument may be of value to other investigators.

The actual measurement is a difference in index of refraction between ordinary water and water containing higher concentrations of deuterium oxide. The instrument was calibrated for direct refractive index measurements by potassium chloride solutions and for molal percentage of deuterium oxide by comparison with the corresponding densities. One

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(1) Gilfillan and Polanyi have developed an ingenious method based on the principle of the Cartesian Diver, *Z. physik Chem.*, **166A**, 255 (1933).

division on the drum was found to be equal to 0.0106% of deuterium oxide. The drum readings were corrected for the familiar change in the fringe colors with drum setting. In the case of the 40-mm cell it was found that the fringes are symmetrical at a reading of 55 divisions and again at intervals of 50 divisions. Thus from 55 to 105 the color match is made one fringe too high and the number of divisions (14) between the fringes must be subtracted from the reading.[2]

Samples of less than 20% concentration were measured with a 40-mm. cell. Higher concentrations can be handled by accurately diluting a small amount with ordinary water. Shorter cells such as the 10-mm. one with a 9-mm. inset giving a 1-mm. layer will handle the highest concentrations. The minimum quantity for the 40-mm. cell is 1.5 cc. and for the others the amount is correspondingly smaller. The precision of measurement is proportional to the length of cell, that for the 40-mm. chamber being about 0.02%. However, our present calibration for drum readings between 1500 and 3000 is not this precise.

Some precautions are necessary in preparing and handling the samples. A large bottle of redistilled water served as a standard. This was checked frequently by redistillation. Moderately concentrated samples for analysis were distilled in a small glass apparatus directly into the cell. Concentrated samples were distilled in a vacuum apparatus and drained into the cell through a tip on the end of the receiver. In the vacuum distillation the air can be removed by shaking during a preliminary freezing. Care must be observed to keep concentrated samples in water-free air to prevent serious dilution.

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(2) See Gans and Bose, *Z. Instrumentenk.*, **36**, 137 (1916); L. H. Adams, THIS JOURNAL, **37**, 1181 (1915), for a discussion of this phenomenon.

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RECEIVED NOVEMBER 24, 1933 PUBLISHED DECEMBER 14, 1933

THE REFRACTIVE INDEX OF H_2O^{18}, AND THE COMPLETE ISOTOPIC ANALYSIS OF WATER

Sir:

In order to determine the validity of several additive laws in mixtures of H^1H^1O and H^2H^2O it has been necessary to dilute H^2H^2O with different amounts of ordinary water. The density of these mixtures and the refractive index, as well as the dependence of the latter upon temperature and wave length, have been determined. The complete results are contained in a paper which has been sent by one of us to the *Physical Review*.

The volumes proved to be not quite additive. When x, which is the mole fraction of H^2H^2O, or the atom fraction of H^2, is 0.50, the molal volume is 0.05% greater than is calculated from linearity, and when $x = 0$ the partial molal volume of H^2H^2O is 0.2% greater than when $x = 1$.

If Δs is the difference in specific gravity at 25° between a given sample and ordinary water, we find that

$$x = 9.579\ \Delta s - 1.03\ (\Delta s)^2 \tag{1}$$

but for less refined work we may write

$$\Delta s = 0.1056\ x \tag{2}$$

Here we have assumed the value Δs equals 0.1056 for pure H^2H^2O given by Lewis and Macdonald [THIS JOURNAL, 55, 3057 (1933)]. If this value is found later to correspond to a different mole fraction than 100% it will suffice to multiply the x given by Equation (1) by that new mole fraction.

The refractive index is found to be linear with the mole fraction. If Δn is the difference in refractive index at 25° between a given sample and ordinary water

$$\Delta n = -0.00449\ x \tag{3}$$

(This is the value for white light as used in an interferometer. The coefficient of x for sodium light is -0.00445.)

From a sample of water containing about 0.5% 0^{18}, and of normal isotopic composition with respect to hydrogen, we have found an approximate value for the refractive index of H_2O^{18}. The effect of this isotope is of the opposite sign from that of H^2, namely

$$\Delta n = 0.0008\ y \tag{4}$$

where y is the increase in mole fraction of H_2O^{18}, or the atom fraction of 0^{18}, over its value in ordinary water. Ordinarily 0^{17} will be too little concentrated to be considered.

We therefore have a remarkably simple method of finding the complete isotopic composition of any sample of water whose density and refractive index have been determined. The equations are

$$x = 1.370\ \Delta s - 190.5\ \Delta n \tag{5}$$

$$y = 7.692\ \Delta s + 180.9\ \Delta n \tag{6}$$

DEPARTMENT OF CHEMISTRY
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GILBERT N. LEWIS
DANIEL B. LUTEN, JR.

RECEIVED NOVEMBER 24, 1933 PUBLISHED DECEMBER 14, 1933

NEW BOOKS

The Elder Pliny's Chapters on Chemical Subjects. In Two Parts. Edited, with Translation and Notes, by KENNETH C. BAILEY, M.A., Sc.D. (Dublin), Fellow of Trinity College, Dublin. Longmans, Green and Company, 55 Fifth Avenue, New York. Part I, 1929. 249 pp. 16 × 24.5 cm. Price, $4.25. Part II, 1932. 299 pp. 16 × 24.5 cm. Price, $5.00.

In an age when scientific knowledge has accumulated to such an enormous extent and when new and astounding scientific discoveries are being made at an ever increasing rate, it is easy to underestimate the scientific knowledge and intelligence of the ancients. These chapters on chemical subjects taken from the "Natural History" of Pliny should serve as an excellent corrective for any such misconception. In them Pliny describes with considerable accuracy and liveliness the properties and either the occurrence and purification, or the manufacture, of a great number of materials—for instance: salt, soda, dyestuffs, sulfur, gypsum, alum, mortar, glass, gold, silver, mercury and other metals, and a host of minerals, earths and "stones," as he called them. The prices and the relative merits of the different sources of supply are given, together with many incidental remarks which disclose the keen mind and the sturdy independence of the author.

These chapters are clearly not the work of any cloistered pedant. Indeed the translator in his Introduction tells us that Pliny was an Augur in his youth and an Admiral of the Fleet at the time of his death. His literary productions were as many and varied, for instance, as those of Priestley. Thus, in addition to the 37 lengthy books of the "Natural History," Pliny wrote a treatise on the "Art of Using a Javelin on Horseback," a "History of the German Wars" in twenty books, "Linguistic Queries" in eight books, and many others.

This is the first separate edition, in English, of these chapters. They will be of interest not only to students of the history of chemistry, but also to teachers of chemistry in general, for their perusal permits us to form a more just conception of the background of our science.

There is one minor feature which will impress the ordinary chemical reader as unfortunate, namely, the necessity of turning continually to a later section of the book to discover and to read the indispensable Notes.

ARTHUR B. LAMB

Second Year College Chemistry. By WILLIAM H. CHAPIN, Professor of Chemistry in Oberlin College. Third edition, revised. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1933. xiii + 374 pp. 40 figs. 15 × 23.5 cm. Price, $3.00.

Since the first printing of the second edition of this book, the author has added a set of 200 problems, transposed the chapters on Homogeneous Equilibrium and Neutralization Indicators, brought forward the chapter on Colloids, and revised or expanded the discussion of the Solubility Product Principle, *P*H and Chemical E. M. F.

This book is primarily intended to serve as the basic text of a second year inorganic course, the first course having included such qualitative analysis as the author considers desirable. This text has been, and continues to be, a pioneer in this arrangement of the chemical curriculum, and it remains one of the very best books for those who follow this arrangement.

"Second Year College Chemistry" may be acceptably employed as a guide to an elementary course in theoretical or physical chemistry for college juniors where a minimum of theory has been introduced with qualitative and quantitative analysis, and where a supplementary course in physical chemistry is given.

In the opinion of the reviewer this book might find some use in supplementing or paralleling a thorough-going course in qualitative analysis, a course which realizes some of the important possibilities that have been neglected in too many courses in this subject, and omitted or inadequately developed in this text, such as, a well-organized study of family relationships through a modern periodic classification based on atomic structure, the relation of modern x-ray crystallography to the nature of solids and solutions, and the significance of different types of valence; the ion association theory, proton chemistry, and the application of these topics to the explanation of different types of reactions, especially in solution.

While commending, in general, the success of the author in preparing a text for the special arrangement of chemical courses he favors, the reviewer is critical of over-emphasis and the tendency in chemical education to introduce prematurely the study of theoretical generalizations at the expense of indispensable knowledge of the facts of chemistry, which can, in part, be acquired through qualitative analysis.

C. R. HOOVER

Fundamentals of Physical Chemistry. By EARL C. H. DAVIES, Professor of Physical Chemistry at West Virginia University. P. Blakiston's Son and Co., Inc., 1012 Walnut St., Philadelphia, Pa., 1932. vii + 370 pp. 78 figs. 15 × 22 cm. Price, $2.75.

The volume is designed to serve as an introductory course in physical chemistry for second year college students having the usual amount of general chemistry and algebra. The author has not written expressly for the student intending to specialize in chemistry, but convinced of the general educational value of the subject, he has aimed to give a broad and comprehensive survey of Physical Chemistry.

The book is well written and covers a wide range of topics in an interesting manner. The objective of the author to prepare the student to understand and profit more fully from all his science courses is well attained.

The first chapters present the usual classical topics, not failing to call to attention, where apropos, the most recent advances. The two principles of thermodynamics receive too brief attention and the periodic law might with advantage have been given a more modern setting. Also the table of isotopes is that of the Table International des Isotopes for 1926. Considering, however, the purpose for which the book was written the author has met the very difficult task of selection of material with insight and a sensitive appreciation of the difficulties confronting the novice in science. The inclusion of photographs of a number of men of science makes a pleasing addition to this attractive book.

F. G. KEYES

Wave Mechanics, Elementary Theory. By J. FRENKEL. Oxford University Press, 114 Fifth Avenue, New York, 1932. viii + 278 pages. 21 Figs., 16 × 24 cm. Price, $5.00.

This book is the first volume of a projected series of three on various aspects of the quantum mechanics; in it are presented the more elementary portions of the theory. The first chapter contains a very suggestive and interesting presentation of the wave-corpuscle parallelism in the case of light, the ideas being developed on the basis of the special theory of relativity. In the second chapter these concepts are extended to matter, and the ideas of wave-packets and probability packets are developed. The third chapter treats of the motion of a particle in a field of force. This includes the approximate solution of a number of one dimensional problems using the "potential-staircase method," in which the actual potential energy is replaced by a simplified potential field. Unfortunately (in the opinion of the reviewer) no use is made of the Wentzel-Brillouin-Kramers approximation method. Chapter III also includes a discussion of transition processes and of electron spin—both rather cursory, as these topics are to be taken up in more detail in later volumes. The latter half of the book is concerned with the motion of systems of particles. The fourth chapter gives an illuminating discussion of this topic from the point of view of the wave mechanics; it leads naturally to the next chapter on statistical mechanics. It should be remarked, however, that the argument of §22 of Chapter IV is not entirely general. The symmetry of $\psi\psi^*$ (top of page 173) will be preserved if a change of particles changes the wave function ψ into its conjugate complex ψ^*, a possibility which is ignored in the discussion. In the last chapter the previously developed principles of statistical mechanics are applied to the theory of electrons in metals. In reading this chapter one is particularly struck with the difference between Frenkel's viewpoint and that of other authors. Much of the development of this chapter is, indeed, the original work of the author, and while one may be inclined to question some of the details, there is no doubt in the mind of the reviewer that the author's point of view is of great interest and value, and it does not appear to have received as much attention from workers in this field as it should have. The reviewer may parenthetically remark, however, that he cannot agree to the validity of the author's treatment of the work function of the metals, it being based on a relation between the electrostatic energy per electron, or per atom, of the whole metal and the work necessary to pull an electron out of the metal, which the reviewer does not believe to be justified.

The unusual point of view and method of presentation, which we have remarked as being particularly characteristic of the last chapter, is by no means confined to that chapter; it runs through the book and makes it particularly stimulating reading. The author always tries to throw light on the various topics presented by viewing them in several different ways. The reader thus sees that the theory is not in a finished state, and is stimulated to think about it. In general, the author tries to show something of the reasoning by which the various results have been obtained, and he often presents partially correct deductions before giving the final one. The beginner should perhaps be warned not to stop when he has read only part of what the author has to say on any subject.

Altogether, the book is one to be heartily recommended, not only to the beginner in the field, but also, and perhaps rather, to those who already have some knowledge of it, which they wish to deepen and broaden.

O. K. RICE

Thermostatica. (**Thermostatics.**) By Prof. Dr. J. E. VERSCHAFFELT, Hoogleeraar te Gent. "De Sikkel," Antwerpen, Belgium; P. Noordhoff N V.. Groningen, Holland, 1933. xvi + 472 pp. 16 × 23.5 cm.

The subject matter of this textbook covers the field of thermodynamics for which the author prefers the more correct though rather uncommon name of thermostatics, relegating the term thermodynamics exclusively to heat transfers in *ir*reversible changes of state. The text is divided into seven parts under the headings: (1) states of matter and changes of state, (2) the energy law, (3) the entropy for reversible changes of state, (4) the entropy for irreversible changes of state, (5) the free energy and the thermal potential, (6) physical equilibria and transformations in mixtures and (7) chemical transformations and equilibria. The discussion is clear, concise and comprehensive. The lack of references to the literature and the absence of an index are defects which will no doubt be corrected in subsequent editions. It is regrettable but probably unavoidable that the author, while on the whole adhering to the custom of European writers on thermodynamics, uses his own system of symbols and nomenclature. Of all the scientists who have made use of Gibbs' monumental contributions to thermodynamics, only his Dutch contemporary van der Waals uses the same symbols for the characteristic functions, ϵ, η, χ, ψ and ζ. Verschaffelt, though a follower of the Dutch school, uses the corresponding notations U, S, W, F and H. The function F is designated, after Helmholtz, as "free energy" while Lewis' free energy (H) is called "thermal potential." W stands for "enthalpy," sometimes spoken of as "heat content" or "total heat" in English and American publications. Although the contributions of German, English, French and American writers are freely quoted, it is only natural that the author devotes considerable space to the notable work of van der Waals and his co-laborers. The applications of thermostatics to chemical equilibria are limited in number but there can be no doubt that any student of physical chemistry who wants to broaden his outlook will profit by a thorough perusal of the text. This book was written to supply the needs of advanced students of mathematical physics and physical chemistry at the only Flemish university in Belgium and is, to the reviewer's knowledge, the first comprehensive treatise in Dutch on thermodynamics. If written in English the text would be of considerable value to English speaking students and it is hoped that the author may, some time, persuade one of his pupils to undertake an English translation.

H. S. VAN KLOOSTER

Organic Chemistry for Medical Students. By GEORGE BARGER, M.A., D.Sc., F.R.S., Professor of Chemistry in Relation to Medicine in the University of Edinburgh. Gurney and Jackson, 33 Paternoster Row, London E.C., England, 1932. xi + 249 pp. 14.5 × 23 cm. Price, 12/6, net.

The circumstance that medical students in the United States have already completed their study of organic chemistry *per se* before entering the medical school, taken in conjunction with the title of this book, is sufficient evidence that there is some difference of opinion within the limits of the English-speaking world as to when and how the subject should be taught to the prospective doctor. The same circumstance inevitably restricts the demand for textbooks of this type in America, but does not in the least alter the fact that Professor Barger's book is a model of its kind. To say merely that it is readable and clearly written is inadequate; the question is whether in that respect it could be improved upon.

Very few typographical errors can be found (*e. g.*, *flour* for *floor* on p. 14), and statements to which exception might be taken are not much more numerous. The brief discussion of methods for the determination of sugar in blood (p. 119) is in part misleading, and something appears to have gone wrong on p. 217, and again on p. 219, for in both places uric acid is said to be converted into urea in lower mammals.

As might be inferred from the above, the book contains no reference to allantoin. All told, a score or more of equally important omissions have been made. Since a book of this character is chiefly useful as a preliminary to a course in animal biochemistry, some mention at least of all comparatively simple organic compounds likely to be encountered in such a course might reasonably be looked for.

In other respects the choice of subject matter is superlatively good. The book can be highly recommended as a text where the subject must be covered in the shortest possible time as part of a crowded medical curriculum. Its scope is, however, too restricted for use in courses in organic chemistry of the kind required for admission to the better medical schools in this country. American medical students may nevertheless in some instances find it of value as a means of brushing up their organic chemistry, or that part of the subject which will be immediately useful to them in connection with their didactic work in biochemistry.

CYRUS H. FISKE

Tannin, Cellulose, Lignin. (Tannin, Cellulose and Lignin.) By Dr. K. FREUDENBERG, Professor at the University of Heidelberg. A second edition of "Chemistry of Natural Tanning Materials." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1933. iv + 165 pp. 14 figs. 17 × 25.5 cm. Price, RM. 8.80.

This treatise is concerned essentially with the fundamental researches carried out by the author and co-workers on the above subject during the last twenty years and the more than one hundred literature references bear witness to Professor Freudenberg's activity and outstanding contributions in these fields.

The student concerned with the developments leading to the establishment of the structural formulas of the natural tannins will find here an excellent and up-to-date account of his work and will be interested in the possible relationship of the tannins to lignin and cellulose as indicated by the author.

The space devoted to cellulose is confined essentially to the author's admittedly outstanding contribution in this field with the consequence that much important work bearing on the establishment of the structure receives little or no consideration.

In the final section of the book Professor Freudenberg gives an account of his researches on lignin and attempts to establish a structure for this very elusive substance. In the reviewer's opinion the conclusions drawn are to be regarded as decidedly problematical and lacking, as yet, the customary rigid, scientific, experimental proof.

The reader interested in obtaining a concise account of the author's valuable accomplishments in the fields indicated will be grateful to him for the opportunity provided in the present volume.

HAROLD HIBBERT

Chemical Embryology. By JOSEPH NEEDHAM, M.A., Ph.D., Fellow of Gonville & Caius College, Cambridge, and University Demonstrator in Biochemistry. In three volumes. The Macmillan Company, 60 Fifth Avenue, New York, 1931. 2021 pp. Illustrated. 16.5 × 24 cm. Price, $35.00.

This scholarly and impressive work in three large volumes attempts and achieves for the first time, so far as I am aware, a thorough presentation of the present knowledge of embryology from the point of view of the chemical changes involved. It should be of the greatest value to the investigator in this field and to the general scientific reader who may wish to secure a broad and yet thorough knowledge of the chemical aspects of embryology.

It will be of special interest to chemists in two respects. First, it shows how important have been the contributions of chemistry to the development of embryology; or expressed in a different way, it demonstrates in a striking fashion the fecundity of the union of the two sciences. The following remarks of the author in his "Prolegomena" in this connection are both interesting and enlivening:

"The Sciences, unlike the Graces or the Eumenides, are not limited in number. Once born, they are immortal, but, as knowledge increases, they are ever multiplying, and so great is now the dominion of the scientific mind that every few years sees a new one brought into the world. Some spring, fully armed, from the brains of one or two men of genius, but most of them, perhaps, come only gradually to their full development through the labours of very many obscure and accurate observers.

"If the analogy may be permitted, physico-chemical embryology has so far been living an intra-uterine existence. Its facts have been buried in a wide range of scientific journals, and its theories have lain dormant or *in potentia* in reviews of modest scope. Physico-chemical embryology has, indeed, arrived at the stage immediately prior to birth, and all it needs is a skilful obstetrician, for, when once it has reached the light of day and has passed for ever out of the foetal stage, it will be well able to take care of itself. This obstetrical task is that which I have chosen and obviously enough it divides into three principal heads: first, to collect together out of all the original papers on the subject the facts which are known about the physico-chemical basis of embryonic development; second, to relate these facts to each other and to the facts derived from the labours of investigators in morphological embryology and 'Entwicklungsmechanik,' and, third, to ascertain whether, from what is at present known, any generally valid principles emerge."

Second, it shows, in its excellent chapters on the history of chemical embryology, that even at the outset chemistry and embryology were closely interconnected both as to subject matter and as to personalities. Thus the chemist will find among contributors to this field such familiar personalities as Albertus Magnus, Robert Boyle, John Mayow and Hermann Boerhaave. Clearly the achievements of these men usually thought of as chemists cannot be properly appraised unless all of their activities are considered.

The first volume, in addition to the history of chemical embryology already mentioned, discusses also what might be called the philosophy of the sciences of chemistry and embryology. It then presents a general discussion of chemical embryology under the heading of The Unfertilized Egg; (1) as a physico-chemical system, (2) its increase in size and weight, and (3) its increase in complexity and organization.

The second volume discusses the respiration and the heat production of the embryo; biophysical phenomena in ontogenesis, and in some 400 pages the metabolism of the embryo from the point of view of its most important chemical constituents.

The third volume discusses the functions of enzymes, hormones, vitamins and pigments in ontogenesis; resistance, susceptibility, serology and immunology in embryonic life, and finally the biochemistry of the placenta, and the blood tissue of the embryo.

In this monumental work the author has marshaled a colossal array of facts into an interesting, suggestive and readable treatise.

ARTHUR B. LAMB

BOOKS RECEIVED

October 15, 1933–November 15, 1933

E. Bougy. "Chimisme de quelques Hybrides de Betteraves." Thèse de Doctorat ès Sciences, Paris, 1933. From the author, l'École Saint-François de Sales, Alençon, France. 76 pp.

L. Ekkert. "Erkennung organische Verbindungen im besondern von Arzneimitteln." Ferdinand Enke Verlag, Stuttgart, Germany. 184 pp. RM. 16; bound, RM. 17.60.

James Murray Luck, Editor. "Annual Review of Biochemistry." Vol. II. Stanford University Press, Stanford Univ., Calif. 564 pp. $5.00.

F. J. Moore. "Outlines of Organic Chemistry. A Book Designed Especially for the General Student." Fourth edition, revised by William T. Hall. John Wiley and Sons, Inc , 440 Fourth Ave., New York. 338 pp. $2.50.

W. O. Pauli and Emmerich Valkó. "Kolloidchemie der Eiweisskörper." Second edition. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 353 pp. RM. 28; bound, RM. 30.

"Gmelins Handbuch der anorganischen Chemie." 8 Auflage. System-Number 8, Iodine. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 415 pp. Mk. 60 to subscribers; singly, Mk. 68.50.

"Mineral Resources of the United States, 1930." Part II, Non-Metals. U. S. Department of Commerce, Bureau of Mines. Superintendent of Documents, Government Printing Office, Washington, D. C. 876 pp. $1.50.

Additions and Corrections

NOTICE TO READERS.—For the convenience of those who may wish to cut out the corrections and attach them to the margins of the articles corrected, they have been printed only upon one side of the page.

VOL. 52, 1930

The Arsonation of Aromatic Aldehydes. By Albert B. Scott and Cliff S. Hamilton.

Pages 4122 ff. "In the article..., solutions of aromatic arsonic acids were warmed with hypophosphorous acid, the characteristic precipitation used as qualitative evidence of arsonation, and this statement occurs: 'When a solution of arsenic trioxide in dilute hydrochloric acid was treated with hypophosphorous acid under these conditions, no precipitate was obtained.' I find that a brown precipitate is formed when arsenic trioxide is warmed with hypophosphorous acid under the conditions described. The original statement is not correct."—ALBERT B. SCOTT.

VOL. 54, 1932

The Heat Capacity and Entropy of Carbon Monoxide. Heat of Vaporization. Vapor Pressure of Solid and Liquid. Free Energy to 5000°K. from Spectroscopic Data. By J. O. Clayton and W. F. Giauque.

Pages 2610 ff. The authors call attention to a small error in calculation and submit corrected data: "In our recent tabulation of the free energy function for carbon monoxide, a small systematic error occurred in the calculation. Also several of the signs were published incorrectly in the equation for rotational energy. Although the error (maximum about 0.04 cal./mole per deg.) is well within the limit of those contributed to the free energy of formation by the heat capacity and combustion data on graphite, it seems desirable to correct the table for future use in reactions where the other data are known with higher accuracy.

$$\epsilon_{\text{rotation}} = \left[1.853 - 0.020\left(v + \frac{1}{2}\right)\right]m^2 - \left[5.418 \times 10^{-6} - 6.918 \times 10^{-8}\left(v + \frac{1}{2}\right)\right]m^4$$

CORRECTED TABLE OF $(F° - E_0°)/T$ FOR CARBON MONOXIDE

T	$-(F°-E_0°)/T$	T	$-(F°-E_0°)/T$	T	$-(F°-E_0°)/T$	T	$-(F°-E_0°)/T$
250	**39.140**	950	48.503	2100	54.476	3600	58.830
298.1	**40.364**	1000	**48.876**	2200	54.843	3700	59.057
300	**40.408**	1050	49.230	2300	55.196	3800	59.278
350	41.479	1100	49.570	2400	55.534	3900	59.495
400	**42.408**	1150	49.896	2500	**55.860**	4000	**59.706**
450	43.228	1200	50.210	2600	56.175	4100	59.903
500	**43.963**	1250	50.513	2700	56.479	4200	60.114
550	44.629	1300	50.804	2800	56.773	4300	60.312
600	45.238	1400	51.359	2900	57.057	4400	60.505
650	45.801	1500	**51.880**	3000	**57.333**	4500	**60.695**
700	46.323	1600	52 370	3100	57 800	4600	60.879
750	**46.813**	1700	52.834	3200	57.860	4700	61.061
800	47.271	1800	53.275	3300	58.112	4800	61.239
850	47.703	1900	53.695	3400	58.358	4900	61.415
900	48.114	2000	**54.095**	3500	**58.597**	5000	**61.586**

The values given in heavy type have been directly calculated. The others interpolated.

The free energy of formation of carbon monoxide at 298.1°K. is −33,000 calories per mole as previously given. The entropy at 298.1°K. is increased by 0.003 to 47.316 calories per mole per degree."—J. O. CLAYTON AND W. F. GIAUQUE.

The Precision with which the Concentration of Solutions of Hydrochloric Acid and Sodium Hydroxide May Be Determined with the Immersion Refractometer. By E. Roger Washburn and Allen L. Olsen.

Page 3216. In the equation at the top of Table II the value "209" should be "229."—E. R. WASHBURN AND A. L. OLSEN.

Quantitative Determination of Calcium by the Magneto-optic Method. By Edna R. Bishop and C. B. Dollins.

Page 4586. In paragraph one, lines 8 and 14, the expression "$1/10^{n+2}$" should be "$1/10^{n}$."—E. R. BISHOP AND C. B. DOLLINS.

The Rate of Reaction between Chlorate and Sulfur Dioxide in Acid Solution. By A. C. Nixon and K. B. Krauskopf.

Page 4606. In the last line change "multiply" to "divide."

Page 4607. Omit Table I. In Table II change μ = 0.033 to 0.33; change the fourth value of k from 2.57 to 2.84, and the fifth value from 2.57 to 2.60, giving a mean value of 2.72.

Page 4608. In the last line change 2.4 to 2.5. —A. C. NIXON AND KONRAD KRAUSKOPF.

VOL. 55, 1933

The Entropy of Polyatomic Molecules and the Symmetry Number. By Joseph E. Mayer, Stephen Brunauer and Maria Goeppert Mayer.

Pages 37 ff. The author writes "Dr. Louis S. Kassel has drawn my attention to an arithmetical error in the paper. In the calculations on acetylene, 4 degrees of freedom at 730 cm.$^{-1}$ contribute 1.1 E. U. at 298°K. The total absolute entropy should be 49.4 E. U. at 298°K. and the practical entropy 46.7, with a possible addition of the 1.1 E. U. due to the vibration at 730 cm.$^{-1}$."—JOSEPH E. MAYER.

Heat Capacity Curves of the Simpler Gases. I. Heat Capacity, Entropy and Free Energy of Gaseous Nitric Oxide from near Zero Absolute to 5000°K. By Herrick L. Johnston and Alan T. Chapman.

Pages 167 ff. "In Table IX, the 'free energy' value at 1125° should read 52.776. Other values in this table, as well as in Table VII of the second paper in this series [Johnston and Walker, THIS JOURNAL, 55, 172 (1933)], deviate from the smooth curve of a large scale deviation plot by 0.001 or 0.002 units and in a few instances by as much as 0.004 unit but, with the correction given above, no values deviate by more than 0.004 unit. This is well below the limits of error (0.01 to 0.04 calories) imposed by other factors, including a small uncertainty in the value of the molar gas constant R."—H. L. JOHNSTON.

The Dissociation of Oxygen to 5000°K. The Free Energy of Atomic Oxygen. By Herrick L. Johnston and Margery K. Walker.

Pages 189 ff. "In Table II, the 'free energy' value for monatomic oxygen at 5000°K. should read 47.637. All other values in this table should be decreased by 0.001 of a unit. In Table III values for K and for α at 298.1°K. should read 1.7×10^{-81} and 2.0×10^{-39}, respectively, while, at 600°, these should read 1.2×10^{-37} and 1.7×10^{-17}, respectively. The last four values in the third column of Table I should read 450.0, 645.5, 45,164, and 96,183, respectively."—H. L. JOHNSTON.

Thermal Equilibrium between Oxygen Molecules and Atoms. By Guenther von Elbe and Bernard Lewis.

Page 508. The last term in equation 8 should read

$$-\frac{1}{2.3R}\left[\int_0^T \frac{C_{\text{vib.}}}{T}\,dT - \frac{\int_0^T C_{\text{vib.}}}{T}\,dT\right]$$

Page 509. The second line, therefore, should read $\int_0^T \frac{C_{\text{vib.}}}{T}\,dT - \frac{\int_0^T C_{\text{vib.}}}{T}\,dT$ can be evaluated by Einstein functions $-(F - F_0)/T$. The numerical values remain unaffected.—GUENTHER VON ELBE AND BERNARD LEWIS.

The Photochemical Reaction between Quinine and Dichromic Acid. II. Kinetics of the Reaction. By George S. Forbes, Lawrence J. Heidt and F. Parkhurst Brackett, Jr.

Page 595. Lines 12 and 13 should read "Over the temperature range 5 to 24° $[(297)^3/(278)^3]^{10/19} = 1.1105$."—GEO. SHANNON FORBES.

Capric Acid from the Seed Fat of the California Bay Tree. By C. R. Noller, I. J. Millner and J. J. Gordon.

Page 1228. At the end of line 11 "caprate" should read "caprylate."—IRVIN J. MILLNER.

The Polymerization of some Unsaturated Hydrocarbons. The Catalytic Action of Aluminum Chloride. By W. H. Hunter and R. V. Yohe.

Page 1248. In this paper "Reference 2 should read *J. Soc. Chem. Ind.*, 49, 349–354 (1930), and in the introduction there should be a reference to Gangloff and Henderson, THIS JOURNAL, 38, 1382 (1916); 39, 1420 (1917).—R. V. YOHE.

The Catalytic Oxidation of Organic Compounds in the Vapor Phase (Book Review). By L. F. Marek and Dorothy A. Hahn.

Page 1302. The authors write: "A review......states that '......there are no author and patent indexes.' The book does have an author index. Through an unfortunate accident the author index was omitted by the publishers from the first copies to be printed. It is possible to obtain this index from the publishers and to insert it in the book with little difficulty, and it would be well for all recipients of these early copies to do this. No patent index was compiled since no effort was made to give a complete review of the patent field and patents were relied upon principally to indicate the industrial trend in certain of the processes which were described."—L. F. MAREK.

The Interconversion of Arylmercuric Halides and Diarylmercury Compounds. II. By R. W. Beattie and Frank C. Whitmore.

Page 1570. Footnote (10) should read "Maynard, THIS JOURNAL, **46**, 1510 (1924)."—FRANK C. WHITMORE.

Addition Compounds of Phenylboric Acid with Bases. By David L. Yabroff and G. E. K. Branch.

Page 1664. In the formulas in the first part of Table I, the second centered period in each case should be a minus sign.

Equilibria, Complex Ions and Electrometric Titrations. I. Iodine or Bromine in Hydrochloric Acid. By J. Horace Faull, Jr., and George Shannon Forbes.

Page 1812. Footnote (9) should read Rây and Sarkar, *J. Chem. Soc.*, **121**, 1449 (1922).—GEO. SHANNON FORBES.

The Calcium Chloride Modifications of Mannose and Gulose. By Horace S. Isbell.

Page 2167. At the end of line 9 the quantity "$-167°$" should be "$-16.7°$."—HORACE S. ISBELL.

Acetylene Polymers and their Derivatives. XV. Halogen-4-butadienes-1,2. The Mechanism of 1,4-Addition and of α,γ-Rearrangement. By Wallace H. Carothers and Gerard J. Berchet.

Page 2810. In the next to the last line the formula "$RMgX(OEt)_2$" should be "$RMgX(OEt_2)_2$."—W. H. CAROTHERS AND G. J. BERCHET.

Addition Reactions of Vinyl Phenyl Ketone. III. Methyl Malonate. By C. F. H. Allen and H. W. J. Cressman.

Page 2960. At the end of line 5 read "3 position" instead of "2 position."—C. F. H. ALLEN.

Organic Reactions with Boron Fluoride. V. The Rearrangement of Isopropylphenol, *o*-, *m*- and *p*-Cresyl Ethers. By F. J. Sowa, H. D. Hinton and J. A. Nieuwland.

Page 3406. Regarding Table I the authors write "We wish to correct the physical constants as tabulated for two phenols in Table I. The physical constants will be correct if 4-isopropylphenol is inserted in place of 2,4-diisopropylphenol and 2,4-diisopropylphenol is inserted in place of 2,4,6-triisopropylphenol. The error was made in the transcription of the data."—F. J. SOWA, H. D. HINTON AND J. A. NIEUWLAND.

The Formation of Cyclic Acetals from Aldehydes or Ketones and Alkylene Oxides. By Marston Taylor Bogert and Richard O. Roblin, Jr.

Pages 3741–3745. The authors write: "Dr. Neal M. Carter of the Pacific Biological Station, Nanaimo, B. C., has called our attention to the fact that certain 1,3-dioxolanes described in our recent paper and which we believed to be new, have appeared in the chemical literature before, as follows. 4-Methyl-2-phenyl-1,3-dioxolane has been described by Gerhardt in German Patent 253,083. He records the boiling point as 113–115° at 14 mm. We found a boiling point of 118° at 23 mm. The 2-methyl-2-phenyl-1,3-dioxolane is covered by French Patent 589,731 and U. S. Patent 1,572,176, by the Société Chimique des Usines du Rhône, where its melting point is recorded as 62°, exactly the same as the figure given in our article."—MARSTON T. BOGERT AND RICHARD O. ROBLIN, JR.

Hydrogenation of Aromatic Compounds at Temperatures Close to their Decomposition in the Presence of Catalysts. By Vladimir Ipatieff.

Page 3696. In text line 13 the temperature given is in centigrade degrees.

Page 3697. The first naphthalene formula is incorrect in that it has two extra carbon atoms.

Pages 3699 and 3700. The accompanying Table II should replace the Table II now on page 3699, and this table should be placed as Table III on page 3700 near the now incorrect reference to Table II in line 15.

TABLE II

NAPHTHALENE

Expt.	Subs., g.	Catalyst	Time, hrs.	Temp., °C.	Pressure, atm. Init.	Pressure, atm. End	Liq.	Tetralin, % no dec., b. p., 195–208°	Benzene HC, % b. p., 80–196°	Naphthenes, % Fr. 80–120°	Naphthenes, % Fr. 120–150°	Analysis of gas % H_2	Analysis of gas % C_nH_{2n+2}
21	150	NiO, 60% Al_2O_3, 40%	11	450	100	39	133	38	47	15	10	81.0	14.5
17	150	MoO_3	12	450	100	42	110	28	53	..	..	78.0	17.2
18	150	MoO_3	12	450	100	47	130	28	..	..	..	..	..
24	250	MoO_3	3	450	100	60	240	76	9	0	0	..	..
25	250	MoO_3	10	475	100	38	205	Cryst.	47	10	0	41.2	58.8
8	100	MoO_3, 50% Al_2O_3, 50%	27	450	65	37	90	29	..	..	..	66.5	28.5
19	150		13	450	100	47	123	26	48	..	..	82.0	15.7
23	250		10	470	100	43	210	Cryst.	46	0	0	60.0	40.0
12	100	CuO, 50% Al_2O_3, 50%	28	450	65	40	64	10	..	0	..	..	..
13	150		28	450	65	42	...	....	..	..	..	..	..
9	50	Fe_2O_3, 50% Al_2O_3, 50%	19	450	65	52	...	....	..	..	..	..	..
10	100		17	450	65	42	142	Cryst.	22	0	..	70.0	26.3
11	100	Fe_2O_3, 50% Al_2O_3, 50%	42	450	65	34	...	....	..	..	..	..	..
26	250	Without catalyst	26	475	100	45	190	Cryst.	47	0	..	53.8	46.2

Page 3701. In line 4, "benzylene" should be "benzene."—VLADIMIR IPATIEFF.

The Common Basis of Intramolecular Rearrangements. II. The Dehydration of Di-*tert*-butylcarbinol and the Conversion of the Resulting Nonenes to Trimethylethylene and Isobutylene. By Frank C. Whitmore and E. E. Stahly.

Page 4157. Regarding line 30, the author writes ". . . the expression 'with an Orsat apparatus' applies only to the isobutylene, the trimethylethylene having first been condensed out and determined by distillation."—FRANK C. WHITMORE.

The Molecular Weight of Linear Macromolecules by Ultracentrifugal Analysis. I. Polymeric ω-Hydroxydecanoic Acid. By E. O. Kraemer and W. D. Lansing.

Page 4323. In line 5 from the bottom, for "$fs = (1 - Vp)/s$" read "$fs = M(1 - Vp)/Ns$."—W. D. LANSING.

The Alkyl Derivatives of Halogen Phenols and their Bactericidal Action. II. Bromophenols. By Emil Klarmann, Louis W. Gates, Vladimir A. Shternov and Philip H. Cox, Jr.

Page 4659. "The phenol coefficient of *n*-amyl-*p*-bromophenol with respect to *Eberthella typhi* is 62.5 (not 625), and that of 4-*n*-propyl-3,5-dimethyl-2-bromophenol with respect to *Staphylococcus pyog. aureus* is 257 (not 357)."—EMIL KLARMANN.

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[1] This index was prepared in the Editorial Offices of *Chemical Abstracts* through the courtesy of Dr. E. J. Crane and under his direction.

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PROCEEDINGS

OF THE

American Chemical Society

1933

EASTON, PA.
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1933

Issued with the January Number, 1933

Proceedings

DIRECTORS' MINUTES

The Directors of the American Chemical Society met at 11 A. M., Friday, November 11, 1932, at the Chemists' Club, New York City, with Charles L. Reese, Chairman of the Board, presiding, and the following Directors present: Roger Adams, George P. Adamson, W. D. Bigelow, Erle M. Billings, Robert T. Baldwin, Arthur B. Lamb, James F. Norris, Charles L. Parsons, Milton C. Whitaker.

Charles L. Parsons was reëlected Secretary and Business Manager; Robert T. Baldwin, Treasurer.

It was voted to defer the issuance of a new Directory of the Society.

A communication from Mr. Martin L. Griffin suggesting certain alterations in Society procedure was read to the Directors. The Secretary was instructed to inform Mr. Griffin that the suggestions he made for changes in Society organization, journals, etc., had been carefully and seriously considered through many months by a general committee of the Society; that the basic problems had been considered by this committee and discussed at two meetings of the Council; and that the Directors feel it is quite impossible to adopt his suggestions and continue the work of the Society for the benefit of the chemical profession.

A proposal from the Editor of *Industrial and Engineering Chemistry* in connection with work on broadcasting under the instructions given him at the Buffalo meeting was approved by the Directors, such approval being subject to such editorial and other control of the project as the Editor of *Industrial and Engineering Chemistry* may direct.

The Treasurer was instructed to utilize the income of the Endowment Fund in 1932 toward the recording of research in the Society's publications during that year.

The Directors instructed the Secretary to express the very sincere appreciation of the Society to the industry for the aid it has given to *Chemical Abstracts*, and to send those whose agreements expire in 1932 the Society's very sincere thanks. The Secretary was further instructed to explain to the industry that while there is no hope of *Chemical Abstracts* being continued for any length of time with real efficiency without the continued help of the industry, the Society feels it must draw on its own reserves in 1933 rather than call for further help from the industry itself under present conditions.

The Directors voted to authorize the Secretary to accept 1933 dues on the instalment plan from those of its members who require such aid on the basis of five dollars down; five dollars additional on or before June 1; and five dollars on or before September 1.

The proposal of the Editor of *Industrial and Engineering Chemistry* to issue the Analytical Edition six times a year instead of four times, as at present, was approved by the Directors.

The proposal from the Editor of *Industrial and Engineering Chemistry* to issue the News Edition once a month, on the fifteenth, instead of twice a month, as at present, was not approved, and an additional amount was added to the budget to continue the News Edition as at present.

After consultation and with the approval of the Paper Committee, the Editor of *Industrial and Engineering Chemistry* proposed the following specifications for the paper used in *Industrial and Engineering Chemistry*, which specifications were approved by the Directors:

> The specifications for the new paper which we propose to use beginning with the January 1st issue of INDUSTRIAL AND ENGINEERING CHEMISTRY differ from the present paper in three respects: (1) Weight; (2) Ash; (3) Finish. The new specifications would then read:

Weight: Basis 25 × 38–45 lbs.; 500 sheets
Stock: 45% sulfite pulp; balance soda pulp
Strength: 12 points, Mullen
Thickness: 0.0030 inch
Color: Uniform white
Ash: 20%
Sizing: Rosin, no starch
Finish: English finish, clear and free from spots.
Pulp must be well washed to remove soluble salts and bleaching material.

The Treasurer was instructed to continue payments to the Editor of *Chemical Reviews* and his assistant as at present, the amounts to be covered by royalty receipts from that publication.

The following budget was then adopted by the Directors:

ESTIMATED INCOME
1933

Dues	$235,000.00
Subscriptions	36,000.00
Back Numbers	3,000.00
Reprints	9,500.00
Postage	9,000.00
Interest	20,000.00
Interest from Endowment Fund	4,500.00
Royalties, net	1,500.00
Advertising	98,000.00
Decennial Index, Sales and Fund	2,120.00
Total Income	$418,620.00
From Reserve to balance	73,029.50
Total	$491,649.50

EXPENDITURES
1933

Journal of the American Chemical Society	$ 73,581.50
Chemical Abstracts	180,954.00
Third Decennial Index	1,920.00
Industrial and Engineering Chemistry, Inc., Analytical Edition	95,360.00
News Edition	20,150.00
News Service	8,790.00
Secretary and Business Manager's Office:	
Secretarial	15,100.00
Business Management	24,434.00
Treasurer's Office	5,060.00
President's Office	1,200.00
Printing Reprints	12,500.00
Printing Advertising	30,200.00
Advertising Development	3,525.00
Scientific Monographs	1,000.00
Technologic Monographs	875.00
Back Numbers	2,000.00
Local Sections	12,000.00
Incidentals	1,500.00
General Meetings	1,500.00
Total Budget	$491,649.50

CHARLES L. PARSONS, *Secretary*

COUNCIL

The following communication was sent to the Council on November 25, 1932:

Councilors of the American Chemical Society:

The following members have been nominated for the offices indicated for the years 1933, 1933–1935, inclusive, and 1933–1936, inclusive. Kindly check your choice with an X and return in the enclosed ballot envelope. Ballot is void unless received on or before December 15, 1932. By vote of the Council, the names are arranged in alphabetical order.

CHARLES L. PARSONS, *Secretary*

President-Elect: 1933 only. (One to be chosen.) Edward Bartow, Oliver Kamm, S. C. Lind, Charles L. Reese.

Councilors-at-Large: 1933–1935, inclusive. (Four to be chosen. Ballot is void unless four are voted for.) James B. Conant, Wm. L. Evans, H. T. Herrick, John Johnston, Charles A. Kraus, John L. Parsons, Alexander Silverman, David Wesson.

Directors: 1933–1935, inclusive. (Vote for one Director in each of the following geographical districts.) First District: (Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut and Canada) James F. Norris. Third District: (Pennsylvania, Delaware and Ohio) Charles L. Reese, Frank C. Whitmore.

Director-at-Large: 1933–1936, inclusive. Selection of Nominating Committee. Vote for one. J. Bennett Hill, M. C. Whitaker.

The returns of this ballot were counted December 15 by a committee consisting of W. D. Bigelow, H. E. Howe, and Charles L. Parsons, and the following officers were elected:

President-Elect: Charles L. Reese.

Councilors-at-Large: James B. Conant, John Johnston, Charles A. Kraus, David Wesson.

Directors: James F. Norris, Frank C. Whitmore.

Director-at-Large: M. C. Whitaker.

CHARLES L. PARSONS, *Secretary*

MEMBERS ELECTED BETWEEN SEPTEMBER 15 AND DECEMBER 15

AKRON SECTION

Cheyney, LaVerne E.
Willson, Edward A.

ARIZONA SECTION

Bast, Waldo L.

CENTRAL PENNSYLVANIA SECTION

Parson, Wm. R., Jr.
Thomas, Joseph J.

CENTRAL TEXAS SECTION

Griffin, L. I., Jr.

CHICAGO SECTION

Eisenstaedt, Edgar I.
Helgren, Fred J.
Shanklin, Wilmetta B.
Simons, L. G.
St. Cyr, Harvey

CLEVELAND SECTION

Soltzberg, Sol
Tramer, Gilbert

COLUMBUS SECTION

Caldwell, John R.
Compton, Jack
Detling, Kenneth D.
Haniewich, Fred Jay
Magill, Mary A.
Paine, Phoebe
Purinton, John A., Jr.
Swan, Donald R.
Whitlock, Douglas L.

CONNECTICUT VALLEY SECTION

McClelland, John R.

CORNELL SECTION

Platenius, Hans

DELAWARE SECTION

Blatz, Peter A.

DETROIT SECTION

Ashraf, F. A.

ERIE SECTION

Kolasa, John J.
Stewart, W. J.

INDIANA SECTION

Kieweg, Homer
McClelland, Earl F.

IOWA SECTION

Buchanan, Marion A.

KANSAS CITY SECTION

Jackson, Merle M.

LOUISIANA SECTION

Foster, Philip
Gunn, Jos. W.
Molaison, Henri J.
Odenheimer, S.

MARYLAND SECTION

Ball, Eric G.
Onderdonk, P. B.
Richardson, Edwin M.

MILWAUKEE SECTION

Helmer, Raymond G.

NASHVILLE SECTION

Baltzly, Richard

Nebraska Section

- Brackenbury, John M.
- Vessel, A. J.

New Haven Section

- Smith, Elizabeth Robison B.

New York Section

- Bissinger, H. Gerard
- Botti, Edmond Charles
- Brous, Calvin
- Caruso, Theodore E.
- Flexser, Leo A.
- Fuller, George H.
- Kassell, Beatrice
- Keith, P. C., Jr.
- Kimball, Frank T.
- Meyer, H.
- Missbach, Lewis E.
- Prange, Charles H.
- Ruderman, Edward
- Russell. Kenneth L.
- Simpson, George J.
- Stanley, Joseph
- Ungar, Stephen

North Carolina Section

- Campbell, Jean I.

Northeastern Section

- Bennett, Emmett
- Bickel, Charles L.
- Childs, Hazel M.
- Handschumaker, Edward
- Klein, Carol
- Lockwood, Maurice H.
- Morgan, Vincent E.
- Nelson, W. Campbell

Northeast Tennessee Section

- Ellis, James

North Jersey Section

- Alexander, William P.
- Ozias, Ramon E.
- Zimmerman, J. B.

Philadelphia Section

- Kent, Russell H.
- Konkle, C. T.
- Lee, Russell
- Viljoen, J. A.

Purdue Section

- Donaldson, Walter E.
- Hanafourde, John K.
- Jensen, Carl C.

Southeastern Texas Section

- Barron, J. Mason
- Douthett, William L.
- Enquist, Melvin A.
- Vaughan, Herschel M.

St. Joseph Valley Section

- Rich, Ronald E.

St. Louis Section

- Fahey, R. J.
- Meyer, H. Sigmund

University of Illinois Section

- Walmsley, C. R.

University of Michigan Section

- Cook, G. A.
- Liao, W. I.
- Merkus, P. J., Jr.
- Redniss, Alexander
- Wynkoop, Everett E.

Washington Section

- Dyer, Helen M.
- Kurtz, Floyd E.

Washington-Idaho Border Section

- Linford, Henry B.

No Section

- Ackerman, Herbert
- Chao, T. Y.
- Child, Reginald
- Coffman, Robert E.
- Floutz, Vaughn W.
- Geisler, J. George
- Gieger, M.
- Hartman, H.
- Hindson, Theodore Phillip
- Ivannikov, P.
- Lant, Alfred
- Roberts, Richmond J.
- Steel, James K.
- Ulmen, Conrad W.

Proceedings

Report of the Editor of Industrial and Engineering Chemistry

In 1932 *Industrial and Engineering Chemistry* appeared in three editions. Volume 24 of the *Industrial Edition* contained 1464 pages, not including tables of contents and "Listening Post" pages, the *Analytical Edition* 454 pages, and the *News Edition* 322 pages. The "Listening Post" is a page devoted to a brief summary of the issue and has proved itself useful in promoting reader interest. Changes in typography, the better use of illustrations, and other details tended to improve the readability of the journal and in general its appearance.

More new manuscripts were received for consideration than in 1931, and a considerably smaller percentage was accepted for publication. A factor in this is that frequently a manuscript reporting good work is found more suitable for some other publication.

As heretofore, many articles have been reprinted from our pages by the technical and trade press, and frequently they are found of sufficient current news value to be recognized by reference in the daily press. The large quantity of manuscripts received—a total of 718 in 1932—obviously requires even more coöperation on the part of our reviewers than heretofore, and to all these we are very grateful.

H. E. Howe, *Editor*

Report of Director of A. C. S. News Service

The amount of space now devoted to creative chemistry in the newspapers of the world is enormous and in large measure this is directly due to the efforts of the American Chemical Society and the activities of its News Service. In addition to the publicity given a specific piece of research and its application, the daily papers carry a vast amount of material in which chemistry plays a major part but which would not ordinarily be classed as publicity for our science. We refer, for example, to pages dealing with food discussions, with health, and with the financial and business side of chemistry. The News Service singles out special researches and endeavors to report them representatively. The application of chemistry to business, to industry, to finance, and to the home is pointed out and we publicize chemistry meetings and chemistry personalities.

We are very careful in the news work to avoid extravagant statements and sensational display. The releases issued by the News Service are uniformly dignified and chemically correct. In addition to nation-wide publicity for national events, our News Service also assists in publicizing discoveries and achievements of local and regional interest and wherever possible has been helpful in the publicity work of our local sections. Many of the releases furnished to the press, besides being immediately useful to it, find a place in the morgue to which the editor may turn on a moment's notice and find material useful in publicizing some important event as, for example, the award of a Nobel Prize.

We believe that in 1932 chemistry made substantial progress in winning general interest and in promoting an ever-widening understanding of its significance. Chemistry has become associated in the lay mind, not merely with colorful theory, but with the realism of practical action. We have reached the place in our work where chemistry penetrates every department of a newspaper and every class of periodical. Our stories are not only to be found in prominent places in papers great and small, but are frequently the basis for constructive editorial comment.

In disseminating our research activities to the press the News Service enlists to a greater extent than ever before the aid of the press associations, the news syndicates, and other news-gathering organizations. This means that chemistry's avenues to the world are continually widening and the work of the News Service takes on even an international aspect.

Because the volume of space accorded to chemistry in the press becomes greater each year, our task has become more selective. The News Service plans its releases for the news pages, financial pages, science pages, as an aid to science editors and commentators, and for other varieties of writing which enter into journalism. From the standpoint of the News Service chemistry is largely synonymous with the Society, which must be viewed as a great central power which constantly works in behalf of the chemist and of the nation. In editorials and other forms of reflective writing inspired by the flow of news, the public is constantly reminded of the American Chemical Society as the source of new knowledge and of social and scientific direction. The chemical laboratory has come to be regarded as a prime factor in national prosperity and happiness and the chemical industry is everywhere looked upon as a vital component of our economic structure, as well as the main reliance of economic progress and stability. We believe that the work of the A. C. S. News Service has been potent in entrenching chemistry and the American Chemical Society in the consciousness of the American nation.

H. E. HOWE, *Director*

Report of the Editor of the Journal of the American Chemical Society for the Year 1932

The number of articles, etc., and the number of pages occupied by them in the several subdivisions of the JOURNAL, during last year and the next preceding four years, are shown in the following table.

	Number					Pages				
	1928	1929	1930	1931	1932	1928	1929	1930	1931	1932
Proceedings..........	...	...	...	...	...	89	82	64	74	68
Physical and Inorganic	237	225	324	247	294	1844	1863	2416	2185	2480
Organic and Biological	250	297	480	344	350	1492	1755	2785	2097	2084
Book Reviews........	68	82	76	103	86	64	71	69	95	88
Communications to Editor.............	...	...	34	77	106	...	...	34	89	107
Indexes, etc..........	...	...	...	...	...	46	47	76	61	70
Total..................................						3535	3818	5444	4601	4897

It can be seen from this table: (a) that, omitting the year 1930 when a special appropriation was made to publish all accumulated material, there has been each year a steady increase in the total number of articles printed; (b) that the number of articles in the Organic and Biological section last year was, as usual, slightly greater than that in the Physical and Inorganic section; and (c) that the number of Communications to the Editor registered a further increase, indicating the growing appreciation of the utility of this type of article.

The average length of the articles, other than Communications to the Editor, published during 1932 was 7.1 pages as compared with 7.2 pages in 1931.

The JOURNAL began 1932 with an accumulated excess of accepted manuscripts equivalent to about 500 printed pages. This excess had been nearly disposed of by

August, but during the summer and early fall an unprecedented influx of new manuscripts occurred so that at the end of the year there was substantially the same excess accumulation as at the beginning. This excess corresponded to a tardiness, as compared with normally prompt publication, of about one and one-half months.

At the end of the year the second terms of Dr. Roger Adams and Dr. E. W. Washburn as Associate Editors expired. Their arduous and unselfish service for ten years on the Editorial Board has been of inestimable value to the JOURNAL, to the Society and to American chemistry. At the Denver Meeting of the Council, Dr. Reynold C. Fuson and Dr. Farrington Daniels, respectively, were elected as their successors.

Respectfully submitted,
ARTHUR B. LAMB, *Editor*

Report of the Editor of Chemical Abstracts for 1932

It is the purpose of *Chemical Abstracts* to maintain a complete record, with adequate indexes, of the literature of chemistry. In accomplishing this for 1932 a new high and a new low mark were struck; more abstracts were published than during any previous year while the average length of abstracts was considerably less than ever before.

The 1932 volume contains 58,081 abstracts. This represents an increase of 6899 abstracts over the total for 1931 (51,182 abstracts). As explained in last year's report the 1931 total does not serve as a true measure of productivity for the year because of "held-over" abstracts. The 1930 total was 53,977 abstracts and the increase for 1932 over 1930 (4104 abstracts for the two years) gives a more accurate indication of chemical literature growth. The occurrence of growth in these times when the general tendency of affairs is strongly in the other direction is to be attributed, we believe, to the fact that the graduate schools are crowded and to the further apparent fact that since research results come slowly there is a carry-over from the rising curve of several years past.

Of the 58,081 abstracts published during 1932, 37,403 are abstracts of papers and 20,678 are abstracts of patents. The corresponding figures for 1931 are 32,278 and 18,904.

The abstracts of papers during 1932 have averaged 0.123 page in length or 8.13 abstracts per page; the average length of such abstracts in 1931 was 0.140 page. This represents a decrease in length of these abstracts of slightly over 12 per cent., a very considerable change (made as an economy measure) in view of the fact that abstracts were already very brief. Patent abstracts in 1932 have averaged 0.065 page in length or 15.38 abstracts per page, exactly the same as in 1931. These abstracts were already so short as to leave little or no opportunity for further abbreviation.

By shortening titles more drastically than usual the 1932 author index has been held to 818 pages, which is 68 pages under the total that might be expected to be needed from the number of abstracts represented. This index was in the mails on December 21st, a new record for promptness made by the printer and index workers.

The edition has been 18,700 copies per number during the greater part of 1932.

With the growth of chemical literature those who buy *Chemical Abstracts*, either by paying dues or the subscription price, have been receiving more each year for the fixed purchase price so that now, if the indexes are counted, they receive over 700 pages of highly concentrated chemical information per month. Abstracts during 1932 were $77^1/_2$ for a cent to subscribers (with 2400 pages of index thrown in) and the rate to members of the American Chemical Society was a good deal better. These are times when we think of things in such terms so it seemed interesting to do a bit of figuring.

New assistant editors for the year are Raymond M. Fuoss, Arthur W. Dox and Homer W. Smith. Doctor Fuoss handled Section 3 ("Subatomic Phenomena and Radiochemistry") during the absence on a trip to Europe of W. Albert Noyes, Jr., last summer and is continuing to help with this section. Doctor Dox, long a maker of very good abstracts, has assumed charge of Section 11A (the "General" subsection under "Biological Chemistry"). Doctor Smith has undertaken to edit Section 11F ("Physiology"), replacing E. K. Marshall, Jr., who gave up the work after helping faithfully during a number of years.

Section 11A had been in charge of Frank P. Underhill for 20 years when death stopped his work on June 28th of last year. He had served as an abstractor before that almost since the beginning of *Chemical Abstracts*. His was a long period of faithful service.

The fine coöperation of all of the abstractors and assistant editors during 1932 is gratefully acknowledged and in particular their good response to our appeals for brevity.

Statistics for the various sections follow:

	1932			
	Abstracts of Papers		Abstracts of Patents	
	No. of pages	No. of abstracts	No. of pages	No. of abstracts
Apparatus and Plant Equipment	42.6	606	66.8	1745
General and Physical Chemistry	422.1	3778	0.2	3
Subatomic Phenomena and Radiochemistry	237.5	2268	1.9	27
Electrochemistry	75.6	652	57.3	1056
Photography	26.6	229	18.4	246
Inorganic Chemistry	74.4	535	....	...
Analytical Chemistry	142.9	1095	1.1	15
Mineralogical and Geological Chemistry	73.8	895	....	...
Metallurgy and Metallography	239.9	2137	127.2	2128
Organic Chemistry	890.0	2984	147.3	1659
Biological Chemistry	998.0	8972	2.4	37
Foods	125.3	1091	22.2	380
General Industrial Chemistry	24.5	386	29.2	446
Water, Sewage and Sanitation	92.0	1015	11.7	239
Soils, Fertilizers and Agricultural Poisons	190.4	1511	30.2	448
Fermentation Industries	42.0	411	13.8	228
Pharmaceutical Chemistry	111.2	1020	36.4	441
Acids, Alkalies, Salts and Sundries	41.0	443	164.1	2339
Glass, Clay Products, Refractories and Enameled Metals	60.9	691	38.0	867
Cement and Other Building Materials	37.8	385	32.6	544
Fuels, Gas, Tar and Coke	131.9	1258	65.4	1113
Petroleum, Lubricants, Asphalt and Wood Products	91.8	893	89.2	1172
Cellulose and Paper	92.4	870	95.4	1510
Explosives and Explosions	22.5	182	8.5	151
Dyes and Textile Chemistry	62.1	740	155.6	1911
Paints, Varnishes and Resins	50.7	511	56.0	768
Fats, Fatty Oils, Waxes and Soaps	54.0	404	18.7	281
Sugar, Starch and Gums	58.4	659	8.4	143
Leather and Glue	39.0	401	10.3	166
Rubber and Allied Substances	49.3	381	41.3	615
Totals	4600.6	37,403	1349.6	20,678
Book titles	59.0	1380		
Headings, blanks and cross references	157.3			

Respectfully submitted,
E. J. Crane

Report of the Secretary and Business Manager of the American Chemical Society for the Year 1932

The Society has held two general meetings during the year: one at New Orleans, La., March 28 to April 1, and one at Denver, Colo., August 22 to 26. Both meetings were successful and larger than anticipated considering the distance from the centers of chemical population. Full programs of these meetings and detailed descriptions of the entertainment and other activities appeared in the *News Edition*, and there will be found therein also an outline of other regional, divisional and local section meetings held during the year. On account of the fact that the membership is kept fully informed through the *News Edition*, this report will be brief.

The membership figures for December 31, 1932, were 18,572, showing a net decrease of 391 below the 18,963 reported for the same date in 1931. This is the first decrease the Society has had to report since the 1921 depression. The membership of the American Chemical Society has held up surprisingly well considering the situation which the members have had to meet. The number of paid members for 1932 has also decreased by an even greater number, the difference being 834. This decrease has been due especially to difficulties with foreign exchange, to reduction in salaries and to unemployment. The number of paid members, however, still is greater by 506 than it was in 1929. The decrease in value of the English pound, Canadian dollar, South American and Japanese currency has forced many of our foreign members to drop their Society membership or to leave their dues unpaid for 1932. Considering the times and particularly the experience of other organizations, the American Chemical Society has fared surprisingly well. In spite of these decreases, and from a financial standpoint the much more important decrease of some $45,000 net advertising receipts, the Society has through the strictest economy, as the Treasurer's report will indicate, again been able to more than balance its budget in 1932. The decrease in advertising receipts is serious and every effort has been made to overcome it. The decrease is small compared with other publications with which the Society usually makes comparisons and is a general situation throughout the country. The Society's expenditures have been carefully studied by the Directors with a view to all possible economy and have been decreased from $548,364.74 in 1930 to $493,387.06 in 1932, as shown by the Treasurer's report for the latter year. The Society's salaries in excess of two thousand dollars have been decreased from five to twenty per cent. on the excess.

The year's chief development has been the incontestable proof that membership is a valuable asset to the individual. Actual unemployment has been less among them than in any non-chemical professional organization of which the Secretary can find record. The unemployment situation has been frequently treated in our publications and may be found summarized on page 63 of the Proceedings for October, 1932. Employers have shown their appreciation of the progressive nature of our membership, and they have been the last to be discharged from employment and are being among the first to be reëmployed. Nevertheless, among chemists, the unemployment situation as a whole is as yet showing little improvement.

The 1933 budget will be found on page 2 of the 1933 Proceedings. It will be noted at once that for the first time in many years expenditures are expected to be in excess of receipts. This is due to the fact that the subsidy of approximately $75,000 a year received during the last five years from the industry and from the Chemical Foundation will be no longer continued. The Directors have, accordingly, voted to draw on the Society reserves in 1933 to the extent of $73,000 in order that our publications may be continued without retardation. While there has been a depression in all lines of business, there has been an actual acceleration in the output of science, which the Society feels it must record and which in recent years has grown by leaps and bounds and is still increasing. The membership will be startled and pleased to realize that when the dues were increased from ten to fifteen dollars in 1921 we printed 9144 pages and that in 1932, without change of dues, we printed 15,390 pages—an increase of 68%. In addition, we are printing and circulating approximately 30% more issues of our publications. It is this increase in membership and increase in subscriptions and, until 1932, increase in advertising receipts that has enabled the Society to continue and expand its work. Until 1932 the Directors have annually budgeted the coming year on the basis of the receipts of the preceding year. As the Society had a constant increase from 1921 until 1932, receipts being greater than estimates, reserves were accumulated, which reserves are sufficient now to carry the Society for two or three years of depression. They were accumulated to meet just such an emergency as that which has arisen. Had they not been accumulated, *Chemical Abstracts* would, in all probability, have to be abandoned at this time. It is hoped and expected that before exhaustion business activity will have returned and we may hope again for the aid of the industry for whom *Chemical Abstracts* is as essential as it is to the individual chemist. Few members realize that they have been, and are, receiving the results of a net expenditure after deducting advertising of over $20.00 for their benefit for every $15.00 they pay in, this subsidy being passed on to our foreign members as well as to those who reside in the United States. Members of the American Chemical Society receive for their dues more than members of any other scientific organization in the world. Compare the cost of our journals to any other chemical journals printed. Three leading German journals are comparable in type and volume to the journals which go to our membership for $15.00. We concede nothing to them in quality although their cost to the chemists of Germany and the chemists of the world is between four and five times the cost of our own three publications. This has been accomplished by American chemists solely on account of their united coöperation and the strength which comes from numbers. If our membership will stand by, pull together, and especially if each member will impress upon every desirable non-member chemist the fact that he should be associated with the work we are doing and that it will be to his advantage to join our organization, the work of our Society will be continued without retardation.

The American Chemical Society prize of $1000, initiated by A. C. Langmuir, was awarded to Oscar K. Rice at the Denver Meeting for his scientific work, as outlined in his address entitled "The Theory of Unimolecular Gas Reactions."

The local sections have been active, details of their meetings being regularly published in the *News Edition*. The Northeast Tennessee Section was chartered in 1932.

The Secretary wishes again to repeat, for the sake of emphasis, the following three sentences.

Employers are more and more coming to realize that one of the greatest sureties of the chemist's attitude of mind to his profession and to his own improvement is membership in the American Chemical Society.

There are few chemists of any prominence or success in America today who are not members of the American Chemical Society.

Any real chemist will find membership in our organization and contact with others of his profession the surest and most efficient of catalysts to success.

Membership in the Society on December 31, 1931, was 18,963. On December 31, 1932, it was 18,572. Statistics follow:

Honorary members	18
Life members	22
Corporation members	476
Members paid, 1932	16,232
Members unpaid, 1932	1,126
Members unpaid, 1931 and 1932	698
	18,572

Accordingly, 698 members were, on January 1, 1933, dropped from membership for non-payment of dues as required by the Constitution but 308 new members began their membership on the same date.

The number of members not in arrears registered in the local sections on November 30, 1931, was 14,787. The number on November 30, 1932, was 14,316. The number in each section for 1931 and 1932 is noted below:

Local Section	Number of paid members, 1931	Number of paid members, 1932	Cash retained from balance, 1931	Total receipts, 1932
Akron	192	173	0.00	192.00
Alabama	75	71	0.00	93.75
Ames	87	89	0.00	75.00
Arizona	32	27	0.00	50.00
California	429	409	0.00	321.75
Central Pennsylvania	94	107	2.14	117.50
Central Texas	78	76	26.51	26.51
Chicago	1106	1022	0.00	829.50
Cincinnati	239	214	0.00	200.00
Cleveland	279	285	0.00	209.25
Colorado	97	94	7.60	82.60
Columbus	173	161	7.18	173.00
Connecticut Valley	171	171	16.80	156.80
Cornell	68	64	3.60	85.00
Dayton	70	62	0.00	87.50
Delaware	323	294	0.00	242.25
Detroit	194	195	0.00	194.00
East Tennessee	43	28	5.00	64.50
Eastern New York	128	130	10.23	128.00
Erie	43	44	0.00	64.50
Florida	81	84	3.37	78.37
Georgia	92	71	29.38	29.38
Hawaiian	30	30	0.92	0.92
Illinois-Iowa	21	20	0.34	34.25
Indiana	194	177	0.00	194.00
Iowa	70	71	0.00	87.50
Kanawha Valley	88	69	0.00	110.00
Kansas City	107	106	0.00	100.00
Kansas State College	26	27	14.33	50.00
Lehigh Valley	150	144	0.00	150.00
Lexington	37	30	0.00	55.50
Louisiana	97	117	0.00	121.25
Louisville	51	51	0.00	63.75
Maine	56	56	18.29	18.29
Maryland	263	270	0.00	200.00
Michigan State College	49	59	0.00	72.50
Midland	68	64	50.00	85.00
Milwaukee	176	150	0.00	176.00
Minnesota	243	250	0.00	200.00
Montana	38	37	0.00	57.00
Nashville	34	34	0.00	51.00
Nebraska	39	36	12.11	58.50
New Haven	126	120	0.00	156.25
New York	1809	1779	76.47	1356.75

Local Section	Number of paid members, 1931	Number of paid members, 1932	Cash retained from balance, 1931	Total receipts, 1932
North Carolina	81	90	0.00	101.00
Northeastern	885	865	0.00	663.75
Northeast Tennessee	...	35	0.00	40.26
Northeast Wisconsin	31	36	0.00	50.00
North Jersey	980	955	0.00	735.00
Northern West Virginia	30	26	1.50	50.00
Northwestern Utah	30	29	3.50	50.00
Oklahoma	146	143	4.00	146.00
Omaha	28	30	0.00	50.00
Oregon	55	51	0.00	68.75
Philadelphia	869	867	0.00	651.75
Pittsburgh	546	497	0.00	325.00
Princeton	45	42	0.00	50.00
Puget Sound	91	91	0.00	100.00
Purdue	56	64	0.00	73.50
Rhode Island	108	103	0.00	135.00
Rochester	197	203	0.00	197.00
Sacramento	37	39	0.00	50.00
Saint Joseph Valley	39	42	0.00	58.50
Saint Louis	272	269	83.94	204.00
South Carolina	23	42	3.40	33.40
Southeast Kansas	35	31	0.25	50.00
Southeastern Texas	89	83	98.99	98.99
Southern California	423	401	0.00	317.25
South Jersey	48	45	0.00	72.00
Syracuse	123	115	0.00	152.75
Toledo	67	58	0.00	83.75
University of Illinois	175	147	4.46	175.00
University of Michigan	98	96	2.93	52.93
University of Missouri	35	37	0.00	52.50
Virginia	154	142	0.00	154.00
Virginia Blue Ridge	41	40	18.18	61.50
Washington, D. C.	508	502	0.00	381.00
Washington-Idaho Border	36	36	0.00	54.00
Western New York	310	307	0.00	0.00
Wichita	33	32	0.00	50.00
Wisconsin	166	157	0.00	166.00
	14,787	14,316	$505.42	$12,654.20
Rebates, account new members secured by local sections	...	...	....	$ 1307.50

The table gives a summary of the sectional accounts for the year, shows the number of members in each local section for 1931 and 1932, the funds held over from 1931 account and the total funds (which include the balance) charged to the 1932 account. It is at once apparent that any savings that can be made by the local sections will immediately aid the general society and the returns which it can make to the membership through its publications.

During the past two fiscal years, December 1, 1930, to November 30, 1932, the Secretary has made the following collections:

	1931	1932
Membership	$264,540.00	$252,190.00
Subscriptions	41,497.62	40,228.61
Back Numbers	4,749.75	3,383.10
Reprints	9,484.80	8,492.30
Postage	11,009.28	9,068.43
Exchange	9.23	8.47
Decennial Indexes	1,247.50	361.00
Directory	165.00	24.00
Chemical Abstracts from Industry	51,725.00	50,165.00
Chemical Reviews' Royalties	920.11	1,187.29
Monograph Royalties	....	1,659.72
	$385,348.29	$366,767.92

These amounts were duly transmitted to the Treasurer of the Society.

Five full sets of *Chemical Abstracts* are now available for sale. A few complete sets of *Industrial and Engineering Chemistry* still remain. No full sets of the *Journal of the American Chemical Society* have been available for some years although of all three journals there are still a number of volumes and single issues in stock as regularly announced in the advertising pages of the Society's journals. The stock is being kept in the best possible condition by the purchase from members and others of the numbers needed to complete full volumes. The ability to furnish back volumes is becoming more and more difficult.

Back numbers are mailed direct from Easton, Pennsylvania, on orders sent through the Secretary's office. The following is the summary of the back numbers sent out by the Secretary during the year, together with the present stock of journals.

Copies of the Society publications sent out from January 1, 1932, to December 31, 1932, aside from mailing lists	58,137
Copies of the *Journal of the American Chemical Society* in stock	22,643
Copies of *Chemical Abstracts* in stock	39,328
Copies of *Industrial and Engineering Chemistry* in stock	16,349
Copies of the General Index, Volumes 1–20, J. A. C. S. in stock	36
Copies of the 25th Anniversary Number in stock	74
Copies of the 50th Anniversary Number in stock	81
Sets of First Decennial Index in stock	27
Sets of Second Decennial Index in stock	1,076

Respectfully submitted,
CHARLES L. PARSONS, *Secretary and Business Manager*

Treasurer's Report

The annual audit of the books of the American Chemical Society has been made, and the audit is herewith respectfully submitted and recommended to your attention.

ROBERT T. BALDWIN, *Treasurer*

Auditor's Report

January 16, 1933.

MR. ROBERT T. BALDWIN, *Treasurer*
American Chemical Society
50 East 41st Street, New York, N. Y.

Dear Sir:

Pursuant to request, we have made an audit of the books and records of the American Chemical Society, as kept by its Treasurer, for the year ending December 31, 1932.

From the above sources of information, we have prepared and herewith submit, the following Exhibits, reflecting the results of our work.

Exhibit

"A"—Condensed General Balance Sheet—as at December 31, 1932.

"B"—Statement of Cash Received and Disbursed During the Year Ending December 31, 1932.

"C"—Statement of Trust Funds, Investments and Cash in Hands of Treasurer or with United States Trust Company, as Trustee, as at December 31, 1932.

The cash in bank was verified by means of checking the amounts recorded as cash received, with the deposits shown by the bank statement. The withdrawals from bank were proven by checking the cancelled checks returned by the bank, with the cash disbursement record. In this manner the balance remaining in bank—subject to check—was determined, and confirmed in writing by the bank. All checks returned from the bank were examined both as to endorsement and correct distribution; we also footed the entries in the cash-book, both as to receipts and disbursements.

We examined and checked all vouchers in support of disbursements, both as to their authenticity and classification.

All Cash Receipts and Disbursements were checked from the cash-book to the respective General Ledger accounts, and all such postings appeared to be in order.

Interest received on securities owned, as well as on securities held in trust, was verified and found to have been properly credited to the respective accounts.

All securities in the custody of the United States Trust Company, as Trustee, were confirmed by written confirmation; all other securities, representing investments of the Society, as well as its Trust Funds (not in the custody of the United States Trust Company), were verified by an actual count, or otherwise properly accounted for.

Title Guarantee and Trust Company—Mortgage Certificate: Our examination in regard to this matter developed the fact that the certificate for $60,000.00, falling due October 31, 1932 was not paid at maturity, although, under an agreement between the Chemical Society and the Trust Company, this certificate was surrendered to the Trust Company, who agreed to pay it in full within the period of grace—18 months. We also found that a similar certificate for $19,000.00, falling due November 1, 1933, was likewise surrendered to the Trust Company, in order to enable them to proceed with the usual foreclosure proceedings.

Respectfully submitted,
F. W. LAFRENTZ & CO.
Certified Public Accountants

AMERICAN CHEMICAL SOCIETY

CONDENSED GENERAL BALANCE SHEET AS AT DECEMBER 31, 1932

ASSETS

INVESTMENTS:

$10,000.00	U. S. Liberty 4th 4¼%, due 1933–1938—Registered......	$ 10,000.00
50,000.00	U. S. Treasury Bonds 4%, due 1944–1945...............	51,432.50
21,000.00	U. S. Treasury Bonds 3⅛%, due 1946–1949.............	20,573.43
25,000.00	U. S. Treasury Bonds 3%, due 1955....................	24,406.27
10,000.00	Federal Land Bank 4½%, due 1933–1943...............	10,150.00
10,000.00	Federal Land Bank 4¼%, due 1937–1957...............	9,987.50
25,000.00	New York State Bonds 3%, due 1956...................	24,372.44
	Mortgages Guaranteed by Title Guarantee and Trust Company:	
	One First Mortgage 5½%, due December 15, 1933.........	45,000.00

Participation Certificates issued by Title Guarantee and Trust Company in 5½% Guaranteed First Mortgages:		
Due October 31, 1932—Proportionate Interest		25,000.00
Due February 14, 1933		30,000.00
Due January 1, 1934		60,000.00
Due March 1, 1935—Proportionate Interest		37,773.36
8 Shares Chemical Foundation, Inc., Capital Stock, Preferred 2 Shares Chemical Foundation, Inc., Capital Stock, Common		1,000.00
Total		$349,695.50
CURRENT ASSETS:		
Cash on Hand—as per Exhibit "B,"	$35,839.27	
Accounts Receivable—Due from Advertisers—Less Reserve	18,779.15	
Interest Accrued on Bonds Purchased December 31, 1932	256.25	
Total		54,874.67
TRUST FUNDS:		
Chemical Abstracts Fund	$46,486.70	
Nichols Medal Fund	3,856.34	
Decennial Index Fund	68,890.74	
Morris Loeb Fund	25,992.25	
Permanent Endowment Fund—(United States Trust Company, Trustee)	97,343.07	
Life Membership Fund—(United States Trust Company, Trustee)	7,112.15	
Priestley Memorial Fund—(United States Trust Company, Trustee)	1,268.58	
Total as per Exhibit "C" (Contra)		250,949.83
TOTAL		$655,520.00

LIABILITIES

TRUST FUNDS—as per Exhibit "C"—(Contra)	$250,949.83
RESERVE for Employees Retirement	50,000.00
BALANCE—Being Excess of Assets over Liabilities	354,570.17
TOTAL	$655,520.00

THIS IS TO CERTIFY that we have audited the records and books of account of the American Chemical Society as kept by its Treasurer, and have prepared therefrom the foregoing Balance Sheet, which is in accord with the Society's books of account, and in our opinion correctly reflects the financial condition of the Society as at December 31, 1932.

All monies received by the Society as donations for specific purposes were found to have been properly credited to the special accounts for which they were contributed.

The Cash in Bank was verified by written certificate from the Depositary, and the Securities held confirmed by actual examination and count.

F. W. LAFRENTZ & CO.
Certified Public Accountants

American Chemical Society

Statement of Cash Received and Disbursed During the Year Ending December 31, 1932

Cash on Hand—January 1, 1932		$ 87,089.34

Receipts

Revenues:		
From Memberships, etc.:		
Dues and Subscriptions	$292,418.61	
Life Memberships	358.50	
Total		292,777.11
From Publications:		
Advertising	$105,595.64	
Back Numbers	3,383.10	
Directory	24.00	
Reprints (Secretary's Office)	8,492.30	
Total		117,495.04
Other Income:		
Interest on Bank Balances	$ 4,993.51	
Interest on Securities Owned	14,911.19	
Total		19,904.70
Miscellaneous:		
Royalties, less $1000 Expense	$ 1,847.01	
Received for Postage	9,068.43	
Principal Received on Maturity of Mortgage Certificate.	20,000.00	
Sundry Items	8.47	
Total		30,923.91
Total		$548,190.10

Disbursements

Publications and General Expenses, Etc.:		
Journal of the American Chemical Society		$ 71,949.24
Chemical Abstracts	$186,388.37	
Less: Appropriation from Chemical Abstracts Fund..	61,388.37	125,000.00
Industrial and Engineering Chemistry		97,938.21
News Edition		14,976.56
News Service		8,816.02
Secretary's Office		16,776.66
Business Manager's Office		26,302.36
Treasurer's Office		5,350.24
Printing Reprints		11,924.95
Printing Advertisements:		
Industrial Journal	$ 28,665.53	
Journal of the American Chemical Society	651.34	
Chemical Abstracts	1,276.27	30,593.14

Advertising Development		2,928.45
Scientific Monographs—Editor's Salary		1,000.00
Technological Monographs—Editor's Salary and Expense		1,013.79
Back Numbers Purchased		1,439.33
Local Sections		12,119.69
Local Section Rebates		1,307.50
General Meetings		1,294.93
Incidentals		511.37
MISCELLANEOUS:		
Contribution to Table of Physical Constants	$ 500.00	
Securities Purchased for Investment	79,352.14	
Interest Accrued on Bonds Purchased December 31, 1932	256.25	
Award for Research to Oscar K. Rice (A. C. Langmuir Fund)	1,000.00	81,108.39
Total		$512,350.83
BALANCE—Cash on Hand—December 31, 1932		35,839.27
TOTAL		$548,190.10

AMERICAN CHEMICAL SOCIETY

STATEMENT OF TRUST FUNDS. INVESTMENTS AND CASH IN HANDS OF TREASURER OR WITH UNITED STATES TRUST COMPANY, AS TRUSTEE, AS AT DECEMBER 31, 1932

CHEMICAL ABSTRACTS FUND.

Investments.	
First Mortgage 5½%, Due November 1, 1933, Guaranteed by the Title Guarantee and Trust Company	$ 19,000.00
Proportionate Interest in Participation Certificate issued by the Title Guarantee and Trust Company in 5½% Guaranteed First Mortgage, Due October 31, 1932	25,000.00
Total	$ 44,000.00

Statement of Cash Received and Disbursed, during the year ending December 31, 1932:		
Cash on Hand—January 1, 1932	$ 556.74	
Receipts:		
Donations and Subscriptions	50,165.00	
Interest from Investments	3,153.33	
From Sale of Proportionate Interest in Mortgage Participation Certificate to the General Investment Fund, Due October 31, 1932	10,000.00	
	$ 63,875.07	
Disbursements:		
Appropriation for Printing Chemical Abstracts	61,388.37	
Balance—Cash on Hand		2,486.70
Total		$ 46,486.70

NICHOLS MEDAL FUND:

As to Corpus:		
Investment:		
30 Shares Allied Chemical & Dye Corporation, Preferred—Par Value		$ 3,000.00
As to Income:		
Cash:		
On Hand—January 1, 1932	$ 736.34	
Receipts:		
Dividends Received from Investment	210.00	
	$ 946.34	
Disbursement:		
Medal Award	90.00	
Balance—Cash on Hand—As to Income		856.34
Total		$ 3,856.34

DECENNIAL INDEX FUND:

Investments:		
$ 5,000.00 U. S. Liberty 1st 4¼%, due 1932–1947 12,000.00 U. S. Liberty 4th 4¼%, due 1933–1938	Cost	$ 17,260.30
Proportionate interest in Participation Certificates, issued by the Title Guarantee and Trust Company, in 5½% Guaranteed First Mortages:		
Due October 31, 1932		10,000.00
Due March 1, 1935		36,234.39
Total		$ 63,494.69
Statement of Cash Received and Disbursed, during the year ending December 31, 1932:		
Cash on Hand—January 1, 1932	$ 3,567.42	
Receipts:		
Donations and Subscriptions	162.25	
Interest on Securities	3,265.38	
Decennial Indexes Sold	361.00	
	$ 7,356.05	
Disbursements:		
General Expenses—evidenced by properly approved Vouchers	1,960.00	
Balance—Cash on Hand		5,396.05
TOTAL		$ 68,890.74

MORRIS LOEB FUND:

Investment:

Proportionate Interest in Participation Certificate issued by the Title Guarantee and Trust Company in a 5½% Guaranteed First Mortgage, Due March 1, 1935	$ 25,992.25

The Income received on the above investment amounted to $1429.58, and was paid over to the Smithsonian Institute, Washington, D. C.

PERMANENT ENDOWMENT FUND: (United States Trust Company, Trustee)

As to Corpus:

Investments:

$10,000.00	Baltimore & Ohio Railroad 1st 4%, 1948	$ 9,787.50
10,000.00	Baltimore & Ohio Railroad 30-year Convertible 4½%, 1960	9,700.00
10,000.00	Detroit Edison Company, General and Refunding 4½%, 1961	10,096.60
10,000.00	Great Northern Railway, General Mortgage 4½%, 1977	9,850.00
10,000.00	New York Central Railroad, Refunding and Improvement 4½%, 2013	10,000.00
12,000.00	Pennsylvania Railroad, General 4½%, 1965	12,282.64
10,000.00	Southern Pacific Railroad, 1st Refunding 4%, 1955	9,762.50
10,000.00	Southern Pacific Railroad, 40-year 4½%, 1969, W/W.	9,900.00
10,000.00	Union Pacific Railroad, 40-year Debentures, 4½%, 1967	10,191.78
		$ 91,571.02

Cash:			
On Hand—January 1, 1932		$ 828.94	
Add:			
Amortization of Premium on Securities—Transferred from Income		17.56	
Balance—Cash on Hand—As to Corpus			846.50
Total—As to Corpus			$ 92,417.52
As to Income:			
Cash on Hand—January 1, 1932		$ 679.06	
Receipts:			
Interest on Bank Balances		332.93	
Interest on Securities		4,040.00	
		$ 5,051.99	
Less:			
Amortization of Premium on Securities:			
Transferred to Corpus	$17.56		
Commission on Collections	108.88	126.44	
Balance—Cash in hands of American Chemical Society			4,925.55
TOTAL			$ 97,343.07

LIFE MEMBERSHIP FUND: (United States Trust Company, Trustee)

As to Corpus:			
Investment:			
$7000.00 New York Central Railroad Refunding and Improvement $4^{1}/_{2}$%, 2013			$ 6,921.25
Cash on Hand—December 31, 1932—(No change during year)			263.79
Total—As to Corpus			$ 7,185.04
As to Income:			
Cash Balance—January 1, 1932—Overdrawn		$ 36.78	
Receipts:			
Interest Received from Investment	$315.00		
Interest on Bank Balances	15.27	330.27	
		$ 293.49	
Disbursements:			
Life Membership Dues	$358.50		
Commission on Collections	7.88	366.38	
Balance—As to Income—Cash Advanced by American Chemical Society			72.89
TOTAL			$ 7,112.15

PRIESTLEY MEMORIAL FUND: (United States Trust Company, Trustee)

As to Corpus:			
Investment:			
$1000.00 New York Central Railroad Refunding and Improvement $4^{1}/_{2}$%, 2013			$ 988.75
Cash on Hand—December 31, 1932—(No change during year)			127.00
Total—As to Corpus			$ 1,115.75
As to Income:			
Cash on Hand—January 1, 1932		$ 210.86	
Receipts:			
Interest Received from Investment		45.00	
Interest on Bank Balances		3.18	
		$ 259.04	
Disbursements:			
Medal Award	$105.00		
Commission on Collections	1.21	106.21	
Balance—Cash in Hands of American Chemical Society			152.83
TOTAL			$ 1,268.58

Summary of Trust Funds

	Investments	Cash	Total
Chemical Abstracts Fund................	$ 44,000.00	$ 2,486.70	$ 46,486.70
Nichols Medal Fund.....................	3,000.00	856.34	3,856.34
Decennial Index Fund...................	63,494.69	5,396.05	68,890.74
Morris Loeb Fund.......................	25,992.25	....	25,992.25
Permanent Endowment Fund.............	91,571.02	5,772.05	97,343.07
Life Membership Fund..................	6,921.25	190.90	7,112.15
Priestley Memorial Fund................	988.75	279.83	1,268.58
TOTAL......................	$235,967.96	$14,981.87	$250,949.83

We Hereby Certify that we have carefully examined the record pertaining to all the foregoing Funds and find that all monies received, or collected, pertaining to said Funds has been credited to the respective accounts to which they properly pertain.

The monies and securities in the custody of the United States Trust Company, as Trustee, were confirmed by written certificates.

All other securities were verified by actual count.

F. W. Lafrentz & Co.
Certified Public Accountants

COUNCIL

President Lamb has appointed H. S. Lukens and Walter T. Taggart the delegates of the American Chemical Society at the Thirty-seventh Annual Meeting of the American Academy of Political and Social Science, April 7 and 8, 1933, at Philadelphia, Pa.

MEMBERS ELECTED BETWEEN DECEMBER 15 AND JANUARY 15

Alabama Section
Ragland, R. C.

California Section
Hoard, James L.
Vaurio, Viljo Walter

Central Pennsylvania Section
Singer, William E.
Trent, Walter R.

Central Texas Section
McDaniel, W. B.

Chicago Section
Adams, Kenneth H.
Cannon, Howard J.
Carman, Edward Welsby
Clements, J. A.
Day, Roland B.
Moffett, Eugene W.

Cincinnati Section
Bergman, Eric A.
Sherman, John K., Jr.

Cleveland Section
Burchfield, Paul E.
Hanzal, Ramon F.
Janssen, W. A.
Kratovila, C. F. L.
Svoboda, Harold F.

Columbus Section
Welling, Charles E.
Winter, Paul K.

Connecticut Valley Section
Anderson, Arnold Frederick
Durbin, Charles G.

Cornell Section
England, C. W.
Miller, Philip A.

Delaware Section
Ortiz, Julien
Slowinske, George A.

Detroit Section
Amundsen, Paul L.
Graves, W. H.
Schwensen, Albert

Florida Section
Hawkins, George A.

Illinois-Iowa Section
Beste, Eugene W.

Indiana Section
Mozingo, Ralph V.
Wantland, Kenneth W.
Weaver, Alfred B.

Iowa Section
Maxwell, Roy D.

Kansas State College Section
Bryson, Leslie M.

Lehigh Valley Section
Butz, Lester C.
Hottle, George A.
Krueger, John
Martin, Harry C.

Maine Section
Cram, Ernest M.

Maryland Section
Anderson, B. E.

Milwaukee Section
Burkardt, L. A.

Minnesota Section
Dorn, John E., Jr.
Rimpila, Charles E.

Nebraska Section
Biswell, Charles B.
Sweet, Leon A.

New Haven Section
Abbiati, Furio Alexander
Horwitt, Max Kenneth

New York Section
Ames, Maurice U.
Barcelon, Jose B.
Caspe, Saul
Damiano, John
Dunn, Edward J., Jr.
Herman, Clarence Richard
Humphries, Earnest Scott
Hurt, Henry H.

Johnston, Cecil E.
Jones, W. H.
Keller, Jacob L.
Lalone, Murray James
Luckmann, Frederick
Rosenthal, Robert
Roth, M. Herbert
Simons, Eric John
Steckler, Samuel P.
Stolzenbach, Charles
Stone, Gilbert C. H.
Trotter, Eugene A.
Troxler, Lindsay B.

NORTHEASTERN SECTION

Bruce, Alfred P.
Chapman, William
Hanson, William E.
Larchar, Trescott B.
Linder, John F., Jr.
Savina, Anthony R.
Smith, Victor Claude

NORTHEAST TENNESSEE

Gillenwater, J. K.

NORTH JERSEY SECTION

Dietz, Walter A.
Drake, Vernon O.
Hall, Samuel L.
Hemming, Charles B.
Hill, William H.
Kitzmeyer, Edmund Leith
Krebs, Henry G.
Nelson, C. G.
Steuber, Henry Noyes

NORTHWESTERN UTAH SECTION

O'Laughlin, John R.

PHILADELPHIA SECTION

Bland, R. E.
Nique, Eleanor
Pearcy, Allen Bernard
Shuman, Harry

PITTSBURGH SECTION

Luedeke, Valentine D.

PRINCETON SECTION

Compton, Walter A.
Lacoss, Donald A.
LaMotte, Ferdinand, 3rd
Miles, Francis T.
Sherman, Albert

PUGET SOUND SECTION

Goss, Warren H.
Houlton, Harold G.

RHODE ISLAND SECTION

Hnizda, Vincent
McAlevy, Ambrose
Milligan, John G.
White, Nelson C.

SACRAMENTO SECTION

Dietrich, William C.
Kleiber, Max

SOUTHERN CALIFORNIA SECTION

Ewing, Marion J.
Teeter, Dwight L.
Volz, John L.

ST. JOSEPH VALLEY SECTION

Bried, Edward A.

ST. LOUIS SECTION

Glass, Henry G.
Still, A. John
Wulfkuehler, Walter

UNIVERSITY OF MISSOURI SECTION

Ashworth, Ural S.
Fourt, Lyman E.

WASHINGTON SECTION

Haskell, Frank B., Jr.
Lakin, Hubert W.
McGinn, Thomas J.
Mountain, John T.
Spies, Joseph R.

WASHINGTON-IDAHO BORDER SECTION

Ruckwardt, Kurt F.

WESTERN NEW YORK SECTION

Harte, Charles Rufus, Jr.
Lipscomb, C. Lloyd
Swentzel, John Paul

WICHITA SECTION

Burroughs, L. C.

WISCONSIN SECTION

Prill, Edward A.

NO SECTION

Cade, George N., Jr.
Drakeley, Thomas J.
Fuchs, Walter
Hanna, Lillian Robina
Harris, George Jordan
Welton, Wright M.
Wilson, William Page
Wintershall Aktiengesellschaft
Yuill, John Lewis

Issued with the March Number, 1933

Proceedings

COUNCIL

MEMBERS ELECTED BETWEEN JANUARY 15 AND FEBRUARY 15

Akron Section

Ford, T. Foster
Good, Don
Walsh, J. M.

California Section

Chesny, H. Henry
Cummings, Ben Henry
Glenn, Dawrence S.
Hicks, J. F. G., Jr.
Holm, M. M.
Johnson, George E.
Schutz, Philip W.

Central Pennsylvania Section

Craig, Kenneth A.
Crooks, Harry M., Jr.
Donelson, John G.
Fowler, Geo. W.
Fulton, George P.
Graeber, Edwin George
James, William H.
Karnatz, Frank Albert
Lewis, H. Richard
Mayberry, M. G.
Stahly, E. E.
Stehman, C. J.
Steinford, Christian H.
Tarr, P. R.

Chicago Section

Artis, William G.
Behrens, Fred V.
Bjerg, Niels Holger
Bradley, Raymond
Christensen, Carl W.
Corbin, Homer B., Jr.
Dyer, William W.
Field, Edmund
Formanek, George
Germain, Louis G.
Gladstone, Martell M.
Lieber, Elmo C.
Lodeski, Frank J., Jr.
Lurie, David
Marlow, Elbert W.
Merriam, Charles J.
Nielsen, Erik R.
Phillips, M. C.
Pijzel, Robert
Schapiro, A.
Schlandt, Arthur F.
Schneider, Herman
Shand, Wilbur Claire

Cincinnati Section

Loofbourow, John Robert
Moomaw, William A.
Rose, Clark B.

Cleveland Section

Cassidy, Philip Edward
Cheney, M. B.
Herrmann, Carl V.
Metcalf, Richard P.

Colorado Section

Turner, James Howard

Columbus Section

Bremer, Clarence
Dominica, Sister Rose
Dudley, Mabel Audrey
Owens, Grafton R.
Pence, Leone
Skeen, Mary I.

Connecticut Valley Section

Howes, William R.
Whiting, William

Cornell Section

Murphy, Nelson F.
Stevenson, Halsey Bidwell

Delaware Section

Lyter, John A.

Detroit Section

Greenberg, Julius
Hahn, Edgar A.
Lesso, Harold F.
Place, Herbert M.

Eastern New York Section

Betz, Margaret D.
McGee, H. B.

Florida Section

Adelson, David E.
Dougherty, Carlton David

Georgia Section

Gresham, Thomas L.
Watkins, Joseph H.

Indiana Section

Campbell, Robyn A.
Riebsomer, J. L.
Tryon, Willard

Iowa Section

Albrook, Raymond L.
Lamb, Vernon A.

Kanawha Valley Section

Hubacher, Max H.
Walworth, Chester A.

Kansas City Section

Dunn, J. Edward
Katz, I. G.
Newby, J. D., Jr.

Lehigh Valley Section

Bernhardt, William Francis
Blank, L. Lawrence
Carrillo, Andres
Dewees, G. Malcolm
Graziani, Orlando
Heiberger, C. A.
Ingols, Heber A.
Johnson, Charles F.
Lieberman, Charles Edward
Nielsen, A. T.
Northup, M. Allen
Pie, Paul F.

Louisiana Section

Davis, R. L.
Isaacs, Marx
Mobley, Roy L.

Maine Section

Curtis, Orman P.

Maryland Section

Ahlberg, J. Elston
Field, Theodore E.
Lundberg, Walter O.
Straughn, J. Lloyd
Wright, Thomas Gorsuch

Midland Section

Shigley, Claire Monroe

Minnesota Section

Miller, Sidney E.
Olson, Richard S.
Piret, Edgar L.
Seljeskog, Sigsbee R.
Webster, Isabella M.
Windus, Raymond F.

Montana Section

Newman, John X.

Nebraska Section

Major, Ralph B.

New Haven Section

Alexeeff, Serge A.
Ross, Arthur N., Jr.

New York Section

Addelston, Aaron
Baum, Herman
Birks, Robert K.
Branscombe, G. H.
Davis, Jeanuot H.
Feinstein, H. I.
Garman, Raymond L.
Gold, George M.
Goldfrank, Max
Haedrich, Vincent William
Hanson, Orville G.
Herrmann, Henriette S.
Johnston, Joseph E.
Keresztesy, John C.
Liotta, Casimiro
Mattice, Marjorie R.
Paltz, Walter J.
Parsons, Dorothy H.
Polger, F. Frank
Shrawder, Joseph, Jr.
Silver, David Franklin
Steffensen, Einar V.
Tenney, Alvan H.
Waldeck, William Francis
Wall, Raymond M.

North Carolina Section

Colehour, James K.
Jones, Ivan D.
Miller, William T., Jr.

North Jersey Section

Andersen, Bjorn
Boese, A. B., Jr.
Grant, Orin B.
Meeker, Samuel
Phragmen, Johan E.
Valjavec, Victor

Northeast Tennessee Section

Bachelder, Charles E.
Quarles, J. Fred
Rigby, J. E.
Smith, Kenneth E.
Zeigler, J. H.

Northeast Wisconsin Section

McCarron, Robert D.

Northeastern Section

Atkinson, Edward R.
Boyce, Elias Burton
Cain, Anne Louise
Chambers, Thomas Seal
Elkins, Hervey B.
Elliot, Robert L.
Graham, Arthur S.
Greene, Delphine D.
Macey, J. Hugh
Nugent, Christopher J.
Ryan, John T.
Sawyer, Herbert LeRoy, Jr.
Sickman, Darrell V.
Wales, Maurice
Walsh, Richard Timothy
Washburn, Walter A.
Weiner, Nathan

Northern West Virginia Section

Corder, Edward M. Wood

Northwestern Utah Section

Goldthorpe, Harold C.
Mursener, Royal C.

Oklahoma Section

Hartley, David D.
Tooke, James W.

Philadelphia Section

Barcus, W. Herman
Bohn, Woodrow Wilson
Bresler, George A.
Bruce, Richard H.
Brunstein, Maurice
Chance, Britton
Dampman, Leroy B., Jr.
Evers, William L.
Hamor, John H.
Hiester, Robert E.
Korpi, Karl John
Lewis, John Arthur
Maeder, Henry G., Jr.
Maister, Hanns
Musgrave, John R.
Pitman, William W.
Raterink, H. R.
Schlimme, Benjamin
Snyder, George H. S.
Widerman, Arnold

Pittsburgh Section

Zink, Robert

Princeton Section

Reid, James A.

Puget Sound Section

Brown, Charles T.
Erwin, Richard P.
Fraser, C. W.

Purdue Section

Cobb, Helen E.
Stoops, Forrest D.
Swank, Howard W.
Weber, Paul

Rhode Island Section

Booth, Robert B.

Rochester Section

Smith, Gregory
Taylor, Erle W.

South Carolina Section

Easley, Joseph H.

Southern California Section

Doherty, Norman F.
Eberz, W. Ferdinand
Levanas, Leo
Mountford, F. H.
Sherman, Jack

St. Joseph's Valley Section

Croxall, Willard J.
Weibel, E. T.

St. Louis Section

Towne, Robert W.

University of Illinois Section

Burton, Alvin A.
Dollear, Frank G.
Doty, J. Roy
Fisher, Henry B., Jr.
Imhoff, C. E.
Kalb, E. William
Munro, Howard E.
Printz, Geo. C.
Whitefort, Robert L.

University of Michigan Section

Ball, Willard James
Benedict, Donald B.
Burwell, Cornelia
Carmichael, Emmett S.
Lovell, F. B.
Wagner, Richard Harman

Virginia Section

Earnest, James Gifford, Jr.

Virginia Blue Ridge Section

Anders, Willard W.
Ward, L. E., Jr.

Washington Section

Bell, R. K.
Fritz, James Clarence
Jessup, Daniel Arthur
Stubbs, J. J.
Ward, George Edward

Washington-Idaho Border Section

Hytowitz, Lawrence David
Miller, Harry

Western New York Section

Georgi, Carl W.
Gould, M. Irwin
Struve, Oscar I.

Wichita Section

Parker, Lloyd
Puckett, Robert E.
Young, Willard

Wisconsin Section

Doak, George Osmore

No Section

Assaley, Alexander George
Beobide, Javier G.
Crawford, Blanche
Duncan, Wallace E.
Fournier, Colonel
van Heiningen, J.
Hoffman, Conrad F.
Horner, Wm. L.
Houben, Josef
Jackson, Charles R.
Kemula, Wiktor
Klotz, A. W.
Logcher, Henri
Mazee, W. M.
Nahas, Kennedy Matthew
Pesce, Lawrence
Philip, James C.
Pollak, Jakob
Riddell, George L.
Rimarski, Walther
Robinson, L. D.
Ronzoni, Luigi
Silhavy, John F.
Snyder, R. B.
Societe Anonyme John Cockerill
Spiker, Harold M.
Teichert, A.
Thieler, Erich
Waller, F. G., Jr.
Weber, Edward T., Jr.
Wilson, John

Proceedings

GENERAL MEETING MINUTES

The Eighty-fifth General Meeting of the American Chemical Society was held in Washington, D. C., Monday, March 27, to Friday, March 31, 1933, inclusive. An account of the meeting will be found in the *News Edition* of *Industrial and Engineering Chemistry* for April 10, 1933.

The Council meeting was held at 9:30 A. M., Monday, March 27, 1933.

On Monday afternoon four general papers, as follows, were presented before the general meeting: "Relation of Chemistry to the State," by Harry L. Derby; "Relation of Chemistry to the Individual," by Charles F. Kettering; "Relation of Chemical to Other Industry," by C. M. A. Stine; "Chemistry—Its Interrelations with Other Sciences," by Hugh S. Taylor.

On Monday evening a dinner with some 400 present, followed by dancing, was held at the Willard Hotel. At this dinner a jeweled Society pin and a purse were presented to Dr. Charles E. Munroe, only living charter member of the Society, as a surprise testimonial to him for his 57 years of service to the American Chemical Society and in recognition of his scientific accomplishments during that period.

On Tuesday evening a reception, entertainment and dance, with music by the United States Marine Band was held at the National Museum with some 2500 persons present.

On Wednesday evening Dr. Irving Langmuir, Nobel Laureate, gave his lecture on "Surface Chemistry," which was followed by a concert by the National Symphony Orchestra, over 3000 persons being present.

All divisions met with the exception of the Leather and Gelatin Division and the Division of Fertilizer Chemistry. Full details of the programs, including titles of papers and addresses, will be found in the *News Edition* for March 20.

The meeting was the largest in the history of the Society. The registration showed 2293 members and guests present. An account of the Council and divisional meetings, together with other data, will be found in the April 10 *News Edition.*

CHARLES L. PARSONS, *Secretary*

DIRECTORS' MINUTES

The directors of the American Chemical Society met on March 26 at 8 P. M. and adjourned at 12:40 A. M., March 27, 1933, in the Willard Hotel, Washington, D. C., with Charles L. Reese, Chairman of the Board, presiding, and the following directors present: Roger Adams, Robert T. Baldwin, W. D. Bigelow, E. M. Billings, A. B. Lamb, Thomas Midgley, Jr., James F. Norris, Charles L. Parsons, Walter A. Schmidt, M. C. Whitaker, F. C. Whitmore, R. E. Wilson.

Charles L. Reese was reëlected Chairman of the Board.

The directors approved an addition to By-Law 17 passed by the Council at the Denver meeting, reading as follows:

> "Subject to the consent of the local section itself, any member of the Society living outside its territory may enroll therein, with full privileges of membership, on payment of $2.00 annually to the local section."

A letter of January 26 to the directors proposing certain modifications in the paper of *Chemical Abstracts* and the *Journal of the American Chemical Society* and unanimously accepted by the directors was approved.

The directors voted that the specifications for the paper in the Society's journals be referred to a committee consisting of F. P. Veitch, B. L. Wehmhoff, H. J. Skinner, the Editor of *Industrial and Engineering Chemistry*, and the Business Manager with power to reword and modify in the interest of simplicity in conjunction with present high paper quality.

A communication was received from the Chairman of the Board of the United States Trust Company of New York under date of March 21, 1933, informing the American Chemical Society that the first five-year period of the Frasch Foundation would end on December 31, 1933, and requesting the Society for an opinion as to the desirability of continuing the present recipients of the fund with especial reference as to whether satisfactory progress has been made by all of such institutions. The letter also informed the Society that the expected income for the next five-year period might be estimated at $25,000 a year. The directors asked that the opinion of Dr. Roscoe W. Thatcher be definitely obtained as to his estimate of the situation as it exists; that the President be empowered to appoint a committee of five competent members of the American Chemical Society to pass on any new projects covering which the United States Trust Company of New York may wish the advice of the American Chemical Society.

The Business Manager having reported that the cost of international postage on our journals was now considerably in excess of the amount charged therefor, he was authorized to increase the postage charge until it more nearly represents the actual cost of delivering our journals to foreign subscribers.

The Treasurer submitted an ad interim report to the directors, which was received and filed.

An ad interim report of the Finance Committee was also presented; was considered by the directors; and was received and filed.

The directors approved the following action of the Treasurer and the Finance Committee covering changes in the Society's securities since the last meeting of the board, November 11, 1932:

Participation Certificates issued by Title Guarantee & Trust Co. in $5^{1}/_{2}\%$ Guaranteed First Mortgages $60,000 due Oct. 31, 1932 and $30,000 due Feb. 14, 1933 have been exchanged for $45,000 cash and interest $5^{1}/_{2}\%$ cash from date of maturities to Feb. 16, 1933 on said certificates, and three new mortgage certificates in the amounts of $5,000, $10,000 and $30,000 at 5%, 5% and $5^{1}/_{2}\%$ and maturities of Feb. 14, 1936, Feb. 14, 1936, Oct. 31, 1935, respectively. These three certificates fit the respective capital structures of the proper accounts and simplify bookkeeping.

The directors approved the following purchase of securities for general investments or reduction of current bank balances:

The proceeds of a participation certificate issued by Title Guarantee & Trust Co. in $5^{1}/_{2}\%$ Guaranteed First Mortgage, amount $21,000 reported in the Finance Committee report of August 20, 1932, as turned in on maturity have been invested in $21,000 U. S. Treasury $3^{1}/_{8}\%$'s 1946/1949 and appears in the auditors' report as the third item of Assets, Exhibit "A," p. 1.

The cash proceeds of the first item in this report have been invested in $45,000 U. S. Treasury $3^{3}/_{8}\%$'s, 1943/1947.

U. S. Treasury 3%'s 1955—$25,000 and appears in the auditors' report as the fourth item of Assets, Exhibit "A," p. 1.

New York State Bonds 3%'s 1956—$25,000, and appears in the auditors' report as the seventh item of Assets, Exhibit "A," p. 1.

U. S. Treasury $4^{1}/_{4}\%$'s dated March 15, 1933, July and December, 1933 maturities—$50,000.

It was voted that the bond of the Treasurer be fixed at $200,000 and that he be authorized to draw on his signature alone, and without restrictions on the Washington, D. C., bank account in the Munsey Trust Company.

On motion duly made, seconded, and carried, the directors (Charles L. Parsons dissenting) authorized the Treasurer, on his signature alone, to establish two additional depositories for the Society's funds in New York City, and that these depositories be the Corn Exchange Bank Trust Company and Irving Trust Company, and that the Treasurer be authorized on his signature alone to deposit and to draw on said new accounts as well as the single current account in the National City Bank in New York City, and to do all things necessary and proper in said matters. The Secretary was instructed under the above motion to certify the following resolutions to the Irving Trust Company and to certify the following resolutions to the Corn Exchange Bank Trust Company of New York City:

"I hereby certify to Irving Trust Company of New York City, that at a meeting of the Board of Directors of the American Chemical Society, a corporation organized under the laws of the State of New York, duly called and held at the Willard Hotel in the City of Washington, D. C., on the 26th day of March, 1933, the following resolutions were duly adopted and are now in full force and effect:

"RESOLVED that Irving Trust Company, of New York City, be designated as a depository of this corporation and that funds of this corporation deposited in said company be subject to withdrawal upon checks, notes, drafts, bills of exchange, acceptances, undertakings or other orders for the payment of money when signed on behalf of this corporation by its following officer, to wit:

TREASURER

"RESOLVED that said Irving Trust Company is hereby authorized to pay any such orders and also to receive the same for credit of or in payment from the payee or any other holder without inquiry as to the circumstances of issue or the disposition of the proceeds even if drawn to the individual order of any signing officer or tendered in payment of such officer's individual obligation.

"RESOLVED that the secretary of this corporation be and hereby is authorized to certify to said Irving Trust Company, the foregoing resolutions and that the provisions thereof are in conformity with the charter and by-laws of this corporation.

"I further certify that there is no provision in the charter or by-laws of said corporation limiting the power of the board of directors to pass the foregoing resolutions and that the same are in conformity with the provisions of said charter and by-laws.

I further certify that the present officers of this corporation are as follows:

NAME	OFFICE
Charles L. Reese	Chairman of the Board
Arthur B. Lamb	President
Robert T. Baldwin	Treasurer
Charles L. Parsons	Secretary

In witness whereof, I have hereunto set my hand as secretary of said corporation and affixed the corporate seal this day of 19 .

Secretary of the Corporation"

"At a meeting of the Board of Directors of the American Chemical Society a Corporation duly organized and existing under and by virtue of the laws of the State of New York held at Washington D. C., on the 27th day of March, 1933, at which a quorum was present, the following resolution was adopted:

" 'RESOLVED, that funds of the Corporation be deposited in the Corn Exchange Bank Trust Company, New York, to be withdrawn by the check, draft, note or acceptance of the Corporation, signed by its

TREASURER

who is hereby authorized to make, negotiate, endorse and assign in the corporate name all checks, drafts, notes, acceptances and other negotiable paper, and all checks, drafts, notes, acceptances and other paper whether in negotiable form or not including letters of credit and warehouse receipts and trust receipts so signed shall be paid by said trust company, and charged to the corporation's account, whether payable to the individual order of said officer or officers so signing, or otherwise, hereby ratifying and approving all that said trust company may do or cause to be done by virtue thereof.'

"I hereby certify that the above is a true copy of the resolution adopted as above stated.

Secretary"

A letter received by the directors from Mrs. Morris Loeb, covering the Morris Loeb Fund, was referred by the directors to President Lamb for consultation with Mrs. Loeb in order to obtain further information and report to the directors.

On motion duly made, seconded and carried unanimously, it was resolved that the President and the Secretary be and they are hereby authorized and directed to do all things necessary and proper so that the Certificate of Incorporation shall be amended by showing the increase of Directors from thirteen, as at present, to fifteen; and furthermore, that the Treasurer be and he is hereby authorized to make the necessary expenditure.

The Treasurer transmitted to the directors a proposition from Dr. Harry Sobotka, Chief of the Laboratories in Mt. Sinai Hospital, covering publication by the Society of "Classics of Biochemistry," the project being outlined in a letter addressed to Robert T. Baldwin, Treasurer, under date of March 12, 1933. The directors requested the Secretary to inform Dr. Sobotka that they regretted there were no funds available that could be used for the purpose.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*

MINUTES OF THE COUNCIL POLICY COMMITTEE

The Council Policy Committee of the American Chemical Society met in the Willard Hotel on March 26, 1933, at 3 P. M., with President A. B. Lamb in the chair and the following members present: Robert T. Baldwin, E. M. Billings, E. J. Crane, G. J. Esselen, Jr., H. E. Howe, Charles L. Parsons, Charles L. Reese, W. A. Schmidt.

It was voted that the Committee felt the resolution presented by the Washington Section should be fully discussed by the Council, but it was the unanimous opinion of the committee that it is unwise at the present time for the Society to adopt this resolution, or any other, bearing upon this matter. A copy of the Washington resolution is preserved in the minutes as a matter of record since it does not appear in the Council minutes. The Council Policy Committee made other recommendations which are to be found in full with action thereon in the Council minutes.

A communication was received from Mr. Charles A. Kraus, Chairman of the Division of Chemistry and Chemical Technology of the National Research Council, regarding the reorganization of that division and asking the American Chemical Society to appoint the six new representatives of the American Chemical Society thereon. President Lamb made the following appointments: Terms to expire July 1, 1934: Edward Mack, Jr., F. C. Whitmore; terms to expire July 1, 1935: M. T. Bogert, A. M. Patterson; terms to expire July 1, 1936: Charles L. Parsons, E. R. Weidlein.

CHARLES L. PARSONS, *Secretary*

COUNCIL MINUTES

The Council of the American Chemical Society met in the Willard Hotel, Washington, D. C., at 9:30 A. M., Monday, March 27, 1933, with President A. B. Lamb in the chair and the following 159 councilors present:

Ex-Officio.—Roger Adams, Wm. D Appel, Robert T. Baldwin, Wilder D. Bancroft, F. E. Bartell, A. S. Behrman, W. D. Bigelow, Erle M. Billings, Marston T. Bogert, J. B. Brown, E. J. Crane, H. W. Dahlberg, A. W. Gauger, H. C. Hamilton, A. J. Hill, H. E. Howe, D. B. Keyes, C. S. Marvel, Thomas Midgley, Jr., E. J. Miller, James F. Norris, W. A. Noyes, Jr., Charles L. Parsons, Charles L. Reese, Walter A. Schmidt, H. A. Schuette, F. W. Sullivan, Jr., Frank C. Whitmore, Robert E. Wilson.

Councilors-at-Large.—James B. Conant, Gustavus J. Esselen, Francis C. Frary, Harry N Holmes, Charles A. Kraus, E. Emmet Reid, E. H. Volwiler.

Local Sections.—*Akron*, H. E. Simmons. *Ames*, Henry Gilman (subs. for R. H. Hixon). *California*, Robert E. Swain (subs. for W. C. Bray). *Central Pennsylvania*, John G. Aston (subs. for Walter Thomas). *Central Texas*, J. R. Bailey (subs. for H. R. Henze). *Chicago*, Howard Adler (subs. for D. K. French), W. H. Bahlke (subs. for W. M. Hinman), Gustav Egloff, W. V. Evans, R. C. Newton, George L. Parkhurst (subs. for B. B. Freud), Adolph E. Schaar, J. J. Vollertsen (subs. for H. I. Schlesinger), K. M. Watson (subs. for S. L. Redman), Walter G. Whitman (subs. for P. N. Leech), P. F. Ziegler (subs. for A. Guilladeau). *Cincinnati*, F. F. Heyroth. *Cleveland*, H. S. Booth (subs. for F. G. Pierce), O. F. Tower, A. C. Zachlin (subs. for N. A. Lange). *Colorado*, Robert C. Lewis (subs. for C. M. Knudson). *Columbus*, Wallace R. Brodie (subs. for C. P. Hoover), Jesse E. Day. *Connecticut Valley*, Emma P. Carr, C. R. Hoover. *Cornell*, E. M. Chamot (subs. for John R. Johnson). *Dayton*, C. S. Adams. *Delaware*, H. A. Lubs, Charles M. A. Stine, E. M. Symmes. *Detroit*, Icie G. Macy, A. B. Scott (subs. for T. A. Boyd). *Eastern New York*, Charles B. Hurd (subs. for A. W. Davison), Roy H. Kienle (subs. for G. M. J. MacKay). *Erie*, D. McC. Sturznickle (subs. for John L. Parsons). *Georgia*, Osborne R. Quayle (subs. for J. S. Guy). *Indiana*, H. E. Barnard (subs. for H. A. Shonle), John H. Waldo (subs. for G. H. Shadinger). *Iowa*, George H. Coleman. *Kanawha Valley*, C. Olin North, *Kansas City*, F. B. Dains. *Lehigh Valley*, R. D. Billinger. *Lexington*, M. Bedford Hume. *Midland*. William J. Hale. *Minnesota*, S. C. Lind (subs. for C. H. Bailey), C. B. Gnadinger (subs. for George Glockler). *Nebraska*, B. Clifford Hendricks (subs. for F. W. Upson). *New Haven*, Stuart R. Brinkley. *New York*, R. A. Baker, Hans T. Clarke (subs. for H. J. Masson), Louis P. Hammett, C. M. Hoke (subs. for Lois Woodford), Martin H. Ittner, D. H. Killeffer (subs. for A. B. Newman), R. E. Kirk, Sidney D. Kirkpatrick (subs. for S. D. Swan), Victor K. La Mer (subs. for C. V. Ekroth), C. S. Leonard, H. Burton Lowe, D. P. Morgan, Jr., Ralph H. Müller, H. C. Sherman (subs. for F. G. Breyer), Foster Dee Snell (subs. for F. E. Barrows), Lincoln T. Work (subs. for R. N. Burns). *North Carolina*, Lucius A. Bigelow (subs. for L. G. Willis). *North Jersey*, Herbert B. Baldwin (subs. for Carleton Ellis), D. L. Cottle (subs. for W. T. Read), M. L. Crossley, Robert J. Moore (subs. for Per K. Frolich), E. C. Pitman, Ralph N. Traxler (subs. for G. M. Maverick), W. F. Tuley (subs. for H. L. Fisher). *Northeast Tennessee*, Martin W. Wadewitz (subs. for C. H. Penning). *Northeastern*, Tenney L. Davis (subs. for S. B. Foster), Gerhard Dietrickson (subs. for M. J. Ahern), Geo. Shannon Forbes, Arthur D. Holmes, Oscar K. Rice (subs. for W. P. Ryan), A. W. Rowe, Wilhelm Segerblom, H. J. Skinner (subs. for K. E. Bell), Raymond Stevens (subs. for Reid Hunt). *Northern West Virginia*, C. A. Jacobson (subs. for Hubert Hill). *Philadelphia*, E. F. Cayo, J. Bennett Hill, Hiram S. Lukens, O. L. Shinn (subs. for H. C. Porter), William Stericker, Walter T. Taggart. *Pittsburgh*, J. D. Edwards (subs. for H. V. Churchill), W. A. Hamor (subs. for L. H. Cretcher), Alexander Lowy (subs. for A. Silverman), William P. Yant (subs. for J. H. James). *Princeton*, N. H. Furman. *Puget Sound*, H. K. Benson. *Purdue*, R. Norris Shreve. *Rhode Island*, Laurence S. Foster (subs. for R. F. Chambers), Frank M. Greenlaw. *Rochester*, Harry LeB. Gray, Willard R. Line (subs. for V. J. Chambers), C. J. Staud. *Saint Joseph Valley*, J. A.

Nieuwland. *South Carolina*, J. E. Mills (subs. for R. N. Brackett). *South Jersey*, Robert E. Rose. *Syracuse*, A. L. Elder (subs. for R. C. Roberts), J. H. Nair. *University of Illinois*, R. C. Fuson, R. L. Shriner (subs. for R. E. Greenfield). *University of Michigan*, H. H. Willard. *University of Missouri*, Herman Schlundt. *Virginia*, Arthur F. Benton, Edwin Cox. *Virginia Blue Ridge*, J. W. Watson. *Washington, D. C.*, J. F. Couch (subs. for H. T. Herrick), R. E. Gibson, Paul E. Howe (subs. for E. W. Washburn), Henry G. Knight, M. X. Sullivan, Edward Wichers. *Western New York*, L. F. Hoyt, Donald M. Kumro (subs. for Paul Brallier), Howard W. Post. *Wisconsin*, C. A. Elvehjem (subs. for Farrington Daniels).

At the request of the President, the Business Manager of the Society gave a brief statement to the Council regarding the unemployment situation and the Society's finances. There have been no decided improvements in employment, although there is a slight change for the better and fewer separations from positions than previously. The American Chemical Society is keeping well within its estimated budget of last December. The Business Manager promises at an early date to publish in the *News Edition* a more detailed statement regarding the present status of the Society's finances so that the membership might be thoroughly conversant with conditions. It is hoped that this statement may be ready for the April 20 *News Edition*.

The names of members deceased since the last meeting were read to the Council, The Council stood for a few minutes in silent tribute to their memory. These names have already been printed in the Proceedings.

The following resolution was presented and unanimously adopted:

> The American Chemical Society at its Council meeting in Washington on March 27, 1933, expresses its most sincere appreciation to the Librarian, the chiefs of divisions and their assistants of the Library of Congress for the great labor and careful attention which they have devoted to the exhibition of rare books, portraits, manuscripts and prints upon the history of chemistry that are being displayed at the Library in commemoration of the two hundredth anniversary of the birth of Joseph Priestley. The artistic display of this material from the Library's priceless collections has impressed all the members of the American Chemical Society with the unexcelled opportunities which the Library of Congress affords for original research upon the origins and historical development of chemistry. The American Chemical Society is also deeply appreciative of the courtesy which the Library has extended to its members in enabling them to visit sections of the Library which are ordinarily not open to the public.

President-elect Charles L. Reese announced that the American Chemical Society Award in Pure Chemistry for 1933 would be made to F. H. Spedding of Berkeley, Calif., at the September meeting of the Society.

The Council adopted the following resolution presented by the Policy Committee:

> Whereas, the scientific bureaus of the Federal Government can render adequate service to the general public only when the highest standards are maintained, and
>
> Whereas, such standards are possible only when personnel is selected with regard to training, experience and oftentimes a peculiar ability in a particular field of investigation;
>
> The Council of the American Chemical Society respectfully petitions the President and Senate of the United States to continue the long-established policy of choosing chiefs of such scientific bureaus solely on the basis of professional and administrative qualifications without regard to political considerations, to the end that such bureaus may perform service of the greatest value in the fields in which they have been established.

The Rochester Section having called attention to the advisability of petitioning Congress to issue a commemorative stamp bearing a likeness of Joseph Priestley to celebrate the bicentennial of his birth, the Secretary was instructed to memorialize the proper authorities.

On recommendation of the Council Policy Committee the following resolution was passed:

> That the Council request each division to appoint a committee to study and report methods for the improvement of programs with special reference to providing for adequate discussion and requiring that no papers be considered for the program unless submitted in manuscript form.

The Council unanimously voted to accept this recommendation.

In harmony with the proposal made at the Denver meeting that the Committee on Policy formulate a schedule for the future meetings of the Society, the committee recommended that each spring it designate regions from which invitations will be considered for the third calendar year in advance. With this in mind, the committee made the following recommendations, which the Council approved, for geographical location of future meetings:

Spring meeting, 1935	New York or New Jersey
Fall meeting, 1935	Pacific Coast
Spring meeting, 1936	Prairie States
Fall meeting, 1936	Western Pennsylvania or Ohio

The Society has on file invitations for the spring meeting of 1935 from the Tulsa and New York Sections, and for the fall meeting of 1935 from the San Francisco Section, but these invitations are unaccompanied by sufficient data to enable the Directors to pass upon them at this time.

By-Laws of the Division of Biological Chemistry of the American Chemical Society adopted by the division at the Denver meeting were found to meet all the requirements laid down in the Constitution and the Council approved their adoption.

Resolutions regarding the support of fundamental scientific research, as proposed by the Washington Section, were presented with the recommendation of the Council Policy Committee that recommendations should be carefully discussed by the Council, but the Committee put itself on record as unanimously of the opinion that neither this resolution nor any other bearing upon the matter should be adopted at the present time. The Washington resolutions were tabled, and Doctor Bogert presented the following substitute motion, which was carried:

> The American Chemical Society, recognizing fully the need of and approving drastic economy in all Government expenditures believe it a duty, as patriotic Americans and scientists, to emphasize the importance of fundamental scientific research to the rehabilitation, progress and prosperity of nations, and to express the hope that this fact will be given the consideration it deserves by industry, municipal, state and federal authorities.

R. W. Thatcher briefly reported the present status of the work conducted during the first five-year period on funds from the Frasch Foundation. This period will be concluded December 31, 1933. The funds allotted have been $20,000 annually to the Boyce-Thompson Institute; $12,000 to the University of Missouri; and $8000 to the University of Wisconsin. There have been two projects at the Boyce-Thompson Institute. The first is the chemistry of insecticidal and fungicidal action. The first part of this study, on lime-sulfur, has been completed, and the second part on pyrethrum, may be completed with the calendar year. The second problem has been the chemical stimulation of plants. While much has been learned the fundamental causes for the reactions observed have not been determined and the project is not likely to be finished under the original grants. At the University of Missouri the project has been on the determination of the energy requirements, or the oxygen consumption, of farm animals, leading to a thermodynamic basis for feeding. At the University of Wisconsin the problem is the biochemistry of nitrogen fixation of legumes. Doctor Thatcher reported important progress in all these studies and indicated that the trustees may request further advice from the American Chemical Society in the not distant future.

After preliminary remarks explaining the situation, Mr. J. H. Nair on behalf of the Syracuse Section, presented the following resolution, which was carried:

> Moved that the recommendation of the Syracuse Section (for a reduction of dues) be referred to a committee of seven, consisting of the President and Secretary and five members to be appointed by the President, two of them members of the Board of Directors and three members of the Council, with instructions to report to the Council at the Chicago meeting in September, 1933, on the advisability of the proposed action, and at their discretion to submit a plan which would make possible financially the continuation of as large a part of our present program as it will merit.

The president appointed, besides the ex-officio members: J. H. Nair (Chairman), T. A. Boyd, E. F. Marsiglio, James F. Norris, R. E. Wilson.

The Council voted that the unexpired term of George P. Adamson, Director-at-Large, be not filled until next fall out of respect to his memory and because of his long and untiring service to the American Chemical Society.

The following reports of Committees were then presented and accepted by the Council:

Advisory Committee to the Bureau of Mines and the Bureau of Standards on Non-Ferrous Metals.—The following subjects were discussed at the meeting, May 11, 1932: (1) Effect of temperature on prop-

erties of metals, (2) Machinability and tool steels, (3) Quenching studies and thermal analysis, (4) Spark testing, (5) Bridge-wire failure, (6) Rail steels, (7) Endurance testing of steel, (8) Properties of cast iron as influenced by superheating in casting, (9) Preparation of pure iron, (10) Gases in liquid metals, (11) Corrosion studies, (12) Unstable alloy systems, (13) Wear of metals, (14) Bearing metals, (15) Thermal conductivity of metallic materials, (16) Precious metals, (17) Screen wire cloth, (18) Molding sands, (19) Casting of aluminum alloys, (20) Shrinkage during casting, (21) Copper-base ingot metals.
Wm. B. Price

Report of Committee on Analytical Reagents, 1932–1933.—The Committee has continued the preparation of specifications for Analytical Reagents which have been published in the *Analytical Edition* of *Industrial and Engineering Chemistry*. At the request of the Committee of Revision of the Pharmacopoeia of the United States of America 1930–1940 an effort is being made to harmonize the requirements for the reagents specified in the Pharmacopoeia and those recommended by the Committee on Analytical Reagents.
W. D. Collins, *Chairman*

Report of the Committee to Coöperate with the Chemical Warfare Service.—Owing to financial considerations a full meeting of the Committee to coöperate with the Chemical Warfare Service was not held during 1932, but several members of the committee individually visited the Arsenal to discuss work in their particular fields. The most important work of the committee was rendered individually by certain members in criticizing and commenting upon preliminary plant design for the manufacture of one of the chemical warfare agents.

Dr. Frank P. Underhill, a valued member of the committee, died during the year and efforts to select a successor have so far been unsuccessful. It is recommended that the committee as now constituted be reappointed. It is expected that the entire committee will be asked to meet together at the Arsenal some time the coming June.
H. E. Howe, *Chairman*

Committee on Hazardous Chemicals and Explosives.—The Committee on Hazardous Chemicals and Explosives wishes to report that it has continued its services during the year as consultant for the Committee on Hazardous Chemicals and Explosives of the National Fire Protection Association.

During the year the Committee has considered the type of containers used for the shipment of potassium and sodium chlorate. In a table entitled "Table of Common Hazardous Chemicals," prepared by this Committee some years ago, under the heading "Usual Shipping Container" wooden barrels were recorded. Since wood is a combustible material, the question was raised whether or not, from the standpoint of safety, metal or steel containers should not be substituted for wooden barrels. A discussion of this question by the Committee disclosed the facts that wooden containers have been satisfactory, and from the standpoint of causing fires and explosions the wooden container has not been a major contributing cause; that the substitution of metal for wooden containers would require the use of a nonrusting material, otherwise particles of rust would contaminate the product, and in case of fires, releases on the metal containers would be necessary, otherwise the containers might explode due to the pressures developed inside the container caused by the liberation of oxygen resulting from the decomposition of the chlorate. The Committee, therefore, concluded that no changes should be recommended at this time.

The members of this Committee recommend that it be continued another year.
G. W. Jones, *Chairman*

Membership Committee—

Individual Members Elected 1932	1437
Corporation Members Elected 1932	19
Members Resigned during the year 1932	1142
Deceased Members 1932	94
Total Membership at end of year 1932	18,572
Members dropped for delinquency on Jan. 1, 1933	698

W. D. Bigelow, *Chairman*

Committee on Standard Apparatus, 1932–1933.—The Committee has continued its coöperation with the Committee on Standardization of the Scientific Apparatus Makers of America. The work during the past year has been confined to consideration of a few minor items of apparatus.
W. D. Collins, *Chairman*

Report of the A. C. S. Representative on the Commission on Standardization of Biological Stains.—A bulletin on "The Visual Spectrophotometry of Dyes," which has been of great service in the analysis of biological stains, was contributed by the Color and Farm Waste Division of the Bureau of Chemistry and Soils.

The progress in the work on the standardization of stains has been retarded during the year 1932–1933 due to the reduction in the staff of the biological stain laboratory of the Color and Farm Waste Division which has, in the past, coöperated extensively with the Commission on Standardization of Biological Stains.

However, the Commission has been able to maintain its research associate at the Color Laboratory, and the routine analyses necessary for the certification of stains have not been impaired. Improvements in these analytical methods have also been reported.
H. T. Herrick

Supervisory Committee on Standard Methods of Analysis.—Nothing has been submitted to the Committee since the last meeting. Therefore there is nothing to report.
H. H. Willard, *Chairman*

Committee on Standardized Methods for Vitamin Research.—Realizing that the policy of the American Chemical Society is to withhold anything in the nature of formal adoption of methods in its name until such methods can be brought to a presumably permanent form, this Committee is making no formal recommendations, in fact has held no formal meetings. Work in the elaboration of vitamin methods has, however, gone forward actively during the past year, and individual members of your committee have taken part in such activities without in any way committing the American Chemical Society. On the whole, it seems to me that this is the best form for the work of this Committee to take in the present state of development of vitamin work.

I shall, of course, be glad to render a fuller report, if desired.
H. C. Sherman, *Chairman*

Committee for the Supervision of the Chemical Engineering Catalog.—The meeting of the Committee for the Supervision of the Chemical Engineering Catalog was held on December 14th. The Chairman of the Committee gave a report on the year's activities and discussed plans for bringing the catalog to the attention of a larger number of chemical engineers who should be very much interested in this publication. Suggestions were also made at the time for increasing the usefulness of this publication.
E. K. Bolton

Committee on Exchanges.—Your Committee on Exchanges has made 19 new exchange arrangements since our last report (made March 8, 1932) and 9 former exchanges, temporarily interrupted, have been resumed. The new exchanges are listed on the attached sheet. As an economy measure 65 exchanges have been discontinued during this period. The total number of periodicals obtained by the Society on the exchange basis is now 635.

The office of *Industrial and Engineering Chemistry* receives 16 of these exchange periodicals and the remainder come to the office of *Chemical Abstracts.*

The Committee maintains exchange arrangements only when periodicals needed in the Society's editorial offices can be more economically or more certainly obtained in that way. Each year the existing exchanges are all reconsidered to see that they are in good order and to determine whether or not continuance is justified. Exchange proposals made to the Committee are often turned down (23 during the past year).

The exchange plan is of great service in the obtaining of papers for abstracting.

E. J. Crane, *Chairman*

Committee on Nomenclature, Spelling and Pronunciation.—In addition to the usual efforts to help individuals and such groups as the Committee on Labels of the Division of Chemical Education with their nomenclature problems, your Committee on Nomenclature, Spelling and Pronunciation has done work during the past year leading to the following decisions:

(1) The symbols Ab and Vi are recommended for alabamine and virginium, respectively, in preference to Am and Va, which were beginning to appear in the literature. Am might be confused as a symbol for "ammonium" or "amyl" and Va as a symbol for vanadium, particularly since there is no "a" in the word virginium. In connection with this decision it should be borne in mind that we were acting only as a nomenclature committee in an effort to be helpful in keeping chemical literature in good form and that our action is not to be construed as having any significance beyond a mere expression of preference for the symbols recommended in so far as the proposed names may be used.

(2) The pure Latin forms (first column below) of the chemical words ending in "-valent" are recommended for use in preference to the Greek-Latin hybrids (second column).

Pure Latin	*Greek-Latin*
nonvalent	
univalent	monovalent
bivalent	divalent
trivalent	trivalent
quadrivalent	tetravalent
quinquevalent	pentavalent
sexivalent	hexavalent
septivalent	heptavalent
octavalent	octovalent
multivalent	polyvalent
covalent	synvalent
equi-valent	isovalent

A study of usage showed that it is overwhelmingly in favor of the words with Latin prefixes for the first 4 valences, while for the higher valences it is more divided, with a slight leaning toward the Greek-Latin hybrids. It is agreed that the desirability of pure forms over hybrids in word construction can easily be overemphasized but with usage so diversified, though in favor of the Latin forms in general, it has seemed desirable to recognize the need for standardization and at least a little better to recommend the pure Latin forms throughout the list. E. J. Crane, *Chairman*

Committee on the Preparation and Publication of a List of Ring Systems Used in Organic Chemistry (Joint with the National Research Council).—The number of known ring systems has increased so rapidly since the work was first undertaken that a reduction of the space allotted to each system has been necessary in order to bring the time of preparation and the size of the published work within reasonable limits. On this scale the manuscript for about half the total number of systems (now estimated at 2500) has been completed, and the question of a contract with the publishers of the Society monographs is now before the Board of Editors. Austin M. Patterson, *Chairman*

Committee on Paper.—In accordance with your request and the usual practice, I am submitting report of the Paper Committee covering the papers used during the past year in the various journals of the Society. The analytical results are enclosed herewith and the specifications for the several papers are also given for comparison.

With reference to the machine finish printing used in the *Journal* and *Chemical Abstracts*, reported under IF. No. 47813, you will note that coniferous wood stock is decidedly lower than called for by the specification; that the acidity is close to neutral, which is an advantage from the durability standpoint; that the alpha-cellulose is practically 72 per cent., which is not bad for a low-priced paper; folding endurance under 500 gram tension is good and the decrease in folding endurance after heating for 72 hours is, I think, as good as could be expected from a paper of this character. Everything considered, I think this is a very good paper of its kind, though the percentage of coniferous chemical wood is very much lower than called for by the specification. This would tend to make this a rather soft sheet which I find is very easily torn.

The results as to stock are in general harmony with those reported last year and there has been no improvement, apparently, in this regard.

The super-calendered printing paper used in *Industrial and Engineering Chemistry* is reported under IF. No. 47814, and you will note that the paper is five pounds light per ream, that the percentage of coniferous chemical wood in the stock is less than half of that called for by the specification and the ash is five per cent high. The *PH* is, I think, satisfactory from a durability standpoint, while the alpha-cellulose is practically 80 per cent. and very good for a paper of this character. The folding endurance both before and after heating is good for paper of this character. The bursting strength is well up. The only point in these results that needs to be emphasized is the low coniferous chemical wood stock.

The cover paper for the *Journal*, reported under IF. No. 47815, is, as you will see, about thirteen pounds per ream light, but it is very much stronger than called for by the specification. Here I think additional weight would be advantageous and would insure greater serviceability of the cover.

The cover paper used in *Chemical Abstracts*, reported under IF. No. 47816, is also about fourteen pounds light per ream and in this case the strength is also way down. I would recommend that the contractor be required to deliver paper meeting the specifications for weight and bursting strength.

The cover paper for *Industrial and Engineering Chemistry*, reported under IF. No. 47817, is about three pounds light per ream, and eight points weak on bursting strength. I think the contractor should be asked to raise the weight slightly and certainly the bursting strength. The covers on this journal rapidly go to pieces in handling.

The cover paper for the *Analytical Edition* of *Industrial and Engineering Chemistry*, reported under IF. No. 47818, is about eight points low in bursting strength and should be raised to specification requirements.

The cover paper for the *News Edition* of *Industrial and Engineering Chemistry*, reported under IF. No. 47819, is slightly lower in weight and less than half as strong in bursting strength as called for by the specification. In this case we either ought to insist that the strength of the paper be that of the specification or lower the specification. I do not believe this paper needs to be as strong as that of the *Analytical Edition* of *Industrial and Engineering Chemistry* but it should comply substantially with specifications.
F. P. VEITCH, *Chairman*

Women's Service Committee, 1932–1933.—The Women's Service Committee is continuing its study of the opportunities for women in chemistry and has had interviews and correspondence with various organizations who have partially covered the ground incidental to other studies, in order to secure what information is already available and thus avoid duplication and save effort

We have hope of an offer of coöperation of one of these organized groups in our study.

A few names have been added to our list of good women speakers.

We have done nothing toward helping the Women's Study Course.

We have had cries of distress from young women in need of employment. Needless to say, we could only reply with a word of hope.

We have had requests from various organizations and colleges for information concerning the future for women in chemistry. We have replied to the best of our ability and are anxious to complete our study so that we may feel that we are giving the best possible answers to the questions that we receive.

We have had comments that this is a poor time to make a study of this sort. We on the contrary believe that a study just at this time will be particularly valuable and will be even more so if followed by a supplementary study in a few years.

The Women Chemists Luncheon at Denver was a great success. Agnes Fay Morgan spoke about her sojourn in Europe with special reference to the positions held and work being done by women in chemistry in various European countries.

The Washington representatives of the Women's Service Committee have for some time had all arrangements made for a dinner for women chemists on the Tuesday evening during the meeting.

In making a recent count the Committee were interested to discover that there are over 800 women members of the American Chemical Society, about 180 of whom have joined during the last $2^1/_2$ years.
GLENOLA BEHLING ROSE, *Chairman*

Committee on Standard Methods for the Examination of Water and Sewage to Coöperate with the Committee of the American Public Health Association.—The Committee wishes to report that it has actively coöperated in the revision of Standard Methods and that a new edition of these methods is now in press. In connection with this work the American Chemical Society Committee has carefully reviewed all chemical methods, corrected manuscripts and galley proof on the new edition.
A. M. BUSWELL, *Chairman*

Report of Editor of Technologic Monographs.—During the year 1932 three technologic monographs were published: Vegetable Fats and Oils by Jamieson, Fixed Nitrogen by Curtis, and Catalytic Oxidation by Marek and Hahn. Two manuscripts have been sent to the printer approved for publication: Action of Refining Agents on Petroleum Products, by Story and Kalichevsky; and Soda Manufacture, by Hou. The monographs on Raw Materials of Lacquer Manufacture by the Paint and Varnish Division, and Arsenical and Argentiferous Copper, by Gregg, Craig and Sillers are now out for review. Thirteen monographs are now being written under contract, some of them long overdue: Carbon by Chaney, Sludge Process of Sewage Disposal by Cramer and Wilson, Sulfuric Acid by Fairlie, Rubber by Hauser, Manganese by McLean, Corrosion of Alloys by McKay, Glass by Morey, Coal Carbonization (revision) by Porter, Furfural by Peters and Brownlee, Carbon Dioxide by Quinn, Electrical Precipitation by Schmidt and Anderson, Aluminothermic Reduction of Metals by Saklatwalla, and Particle Size by Work.
H. E. HOWE

Committee on Industrial Alcohol.—Your committee has not been active and has had no meeting during the past year.

Although the governmental control of alcohol is far from being as free from annoying restrictions to manufacture, sale and use as many manufacturers would like to see it, this control as exercised by the Bureau of Industrial Alcohol is probably as well administered as we can expect under Prohibition Laws.

Looking ahead, Industrial Alcohol finds itself in an uncertain position due both to the economic depression and to the possibility of repeal of the 18th Amendment. It is to be hoped, however, that in the attempts that may be made to effect changes in Governmental Bureaus in the interest of economy, alcohol control will not be shifted from experienced to inexperienced hands, and it is also sincerely hoped that any new legislation that may be enacted because of its bearing on the subject of Prohibition will not treat alcohol as a football and render its control worse instead of better.
MARTIN HILL ITTNER, *Chairman*

Report of the Patent Committee.—During the first session of the 72nd Congress more than a dozen bills of interest to the patent profession were introduced and extensive hearings held. Nearly all of these bills failed to pass.

The Bills which were actually passed and approved during this first Session and which are of interest to the patent profession were only three in number.

Economy Bill, H. R. 11267, increasing the patent fees. Approved June 30, 1932, Public No. 212, 72nd Congress.

S. 4912. To protect foreign exhibitors at the Chicago Fair in their inventions and copyrights. A temporary provision. The Bill was passed without a hearing and approved July 19, 1932. Public No. 294, 72nd Congress.

S. 2173. Providing for recording labels, etc., of labor unions in the District of Columbia. The bill was passed without a hearing and approved February 18, 1932. Public No. 35, 72nd Congress.

During the second session of the 72nd Congress only two of the many bills introduced were passed and approved. The details of those introduced which are of interest will be found in Appendix B.

The only two bills which were passed and approved were the joint resolution relative to the World's Fair at Chicago and H. R. 14363 which included the appropriation for the Patent Office. From the report of the appropriation committee, No. 1890, Jan. 21, 1933 it appears that the Patent Office has been relatively very fortunate in the treatment it has received from Congress. The total appropriation for the Department of Commerce of which the Patent Office is a division was $36,588,465 against $44,784,408 for the present fiscal year or a reduction of 18%, while the Patent Office appropriation has been reduced only 9½% from that for the current year. That this reduction was not unreasonable at the present time of stress and trouble is indicated by the fact that in the past two years patent applications pending, have been reduced from 120,000 to 60,000 and if the number of new patent applications continues to fall off a still further reduction in the appropriation for the Patent Office would probably be justified.

Commissioner Robertson made a very interesting statement in his report to the effect that the cost of printing and binding the Official Gazette and Specifications is costing over $6 per page in the government printing office against $3.77 per page in 1921. The Commissioner says if he were allowed to give the printing to outside bidders that large savings could be made. The magnitude of this waste which was forced on the patent department, may be realized from the fact that the cost of printing and binding was $1,100,000 or 22½% of the appropriation for the entire patent office during the current fiscal year. The Commissioner's suggestion seems such an excellent one that it deserves careful consideration from Congress and from other governmental departments that are now forced to have their printing done by the Government Printing Office.

During the past year one meeting of your Patent Committee was called in New York. The Chairman has had considerable correspondence and conferences with members of the Committee. He desires to express his appreciation of the valuable help given by Mr. Charles H. Potter, your Washington member, who has at all times kept him posted regarding the patent legislative situation in Washington.

HENRY HOWARD, *Chairman*

R. E. Wilson presented the following resolution which the Council adopted:

> Resolved, that in the opinion of the Council it is not in the interest of orderly and intelligent action by the Council for local sections to definitely instruct their Councilors on questions that may come before the Council. Councilors should have the benefit of the discussion and the general opinion of the section, but they should be free to act independently in the light of the opinion of the section, plus all the facts which may be brought out at the Council meeting.

At the suggestion of Mr. Lukens, the Council voted that the American Chemical Society express its appreciation of the gratifying results attained through the efforts of the local section membership committees during the recent period of stress and bespeak their continued coöperation in maintaining the membership enrollment.

A unanimous vote of thanks was passed to the Washington Section; to the chairmen and members of the local committees who made the meeting one of the largest and most successful in the history of the Society; to Dr. C. A. Browne for his successful efforts in conjunction with the authorities of the Library of Congress for the display of historical documents bearing upon the history of chemistry with special emphasis on Priestliana; to the Librarian of Congress and those associated with him in the historical exhibit just mentioned; to Major General H. L. Gilchrist, of the Chemical Warfare Service, and to Colonel C. E. Brigham, commanding officer of Edgewood Arsenal, for their hospitality at Edgewood Arsenal on Friday, March 31, and for the interesting display of the facilities of the Chemical Warfare Service as demonstrated to the visitors at Edgewood Arsenal on that date. The Secretary was instructed to express these thanks to the individuals mentioned.

CHARLES L. PARSONS, *Secretary*

COUNCIL

MEMBERS ELECTED BETWEEN FEBRUARY 15 AND APRIL 15

AKRON SECTION

Armstrong, Talbott V.
Lyons, J. K.
Schoenfeld, Frank K.

CALIFORNIA SECTION

Barthelmess, Dougald F., Jr.
Bonnar, Robert U.
Glass, Maryvee (Miss)
Henn, Woldemar Raymond

CENTRAL PENNSYLVANIA SECTION

Aluise, Veto A.
Bixler, A. L. M.
Longenecker, Herbert E.
Oakwood, Thomas S.

CENTRAL TEXAS SECTION

Biggs, Burnard S.
Roosth, Isadore

CHICAGO SECTION

Conner, Herbert W.
Harnly, J. W.
Kirkbride, Chalmer G.
Monell, Ira H.
Rimmke, Hugo
Schreiber, Richard S.
Sekera, Vladimir C.
Ward, George W.

CINCINNATI SECTION

Irish, Don DeLance

CLEVELAND SECTION

Beadel, R. O.
Dorn, Randolph J.
Jenner, R. Wesley
Roninger, Frank H., Jr.
Steinmetz, Victor

COLORADO SECTION

Burwell, E. Chester
Hill, Frederick G.
Holloway, Judson H.
Recht, Christian F.

COLUMBUS SECTION

Long, Earl A.

CONNECTICUT VALLEY SECTION

Kelsey, Winfield F.
Scheuermann, Carl H.
Stratton, Reuel C.

Cornell Section

Hand, David B.
Manley, Thomas Clinton
Smith, Walton J.

Delaware Section

Grier, Frank R.

Detroit Section

Kloetzel, Milton C.
Mattheus, Albert O.

Erie Section

Clark, A. D.
Clarke, Richard G.
March, Carey E.

Georgia Section

Murray, W. M., Jr.

Hawaiian Section

Cornell, Elton F.

Indiana Section

Cavanaugh, Robert M.
Plummer, William

Kansas City Section

Martin, Wm. H.

Kansas State College Section

Buck, T. M.

Lehigh Valley Section

Chapin, Henry M.
Jackson, Charles M.
Jenny, Ernest F.
Skelly, J. S., Jr.
Winkler, David W.

Louisiana Section

Hinds, Horace, Jr.

Louisville Section

O'Bannon, Loran S.

Maine Section

Plotica, George K.
Wooley, Allan D.

Maryland Section

Cairns, Robert William
Meadown, Jacob Robert

Minnesota Section

Clayton, James O.
Werth, Sister Magna

New Haven Section

Bergmann, Werner

New York Section

Allbee, Charles C.
Auerbach, Louis
Cornelius, Yngve R.
Dodge, William Goss
Dunay, Maurice
DuPuis, Robert N.
Eyerly, Katherine (Miss)
Govett, Thomas
Healy, Frank L.
Hirsch, Joel H.
McLoughlin, Edward T.
Ogden, Albert B.
Rivera, Jose A.
Schutt, Hermann C.
Selin, Walter F.
Wall, Emil
Wills, John H
Zrike, Edward

North Carolina Section

Harwood, Edgar H.

North Jersey Section

Ball, Ralph H.
Bennett, Frank I.
Edwards, David F.
Henry, Sarah E.
Johns-Manville, Inc.
Rector, Philip Robert
Rosenberg, Louis T.
Van Mater, Henry L.
Watkins, Dale I.

Northeastern Section

Mann, Charles V.
Morisani, Eugene A.
Pilcher, Malcolm H.
Prentiss, Spencer S.
Schneider, J. (Dr.)
Sulya, Louis L.
Weymouth, Harold D.

Northeast Tennessee Section

Butler, C. O.
Childs, H. R.
Hofmann, H.
Ruggles, Albert C.

Oklahoma Section

Johnson, R. L.
Pate, Carl L.

Philadelphia Section

Asturias, Oscar
Feick, Bernard R.
Graham, W. E.
King, George J.
Koenig, W. J.
Rasch, Mary Katherine (Miss)
Schmidt-Nickels, Wilhelm (Dr.)
Spiegel-Adolf, Mona (Dr.)

Pittsburgh Section

Bessey, Otto A.

Rhode Island Section

Huey, Robert
Morse, Reginald A., Jr.
Smith, Frank B.

Rochester Section

Gutliph, Earl W.
Sinclair, R. G.
Thompson, Herbert E., Jr.

Southeastern Texas Section

Strong, H. E.

Southern California Section

Hunsaker, Victor H.
Kroesche, H. J.
Nutting, Lee
Tarr, Lloyd N.

South Jersey Section

Mattison, E. L. (Dr.)

St. Joseph Valley Section

Allard, Romeo Paul

St Louis Section

Bowman, Max I.
Fleetwood, Charles W.
Huff, Arthur E.
McCauley, Matthew S.
Siefker, A. J.

Syracuse Section

FitzGerald, Dorothea (Miss)
Hanford, Zaida M. (Miss)
Kelly, Walter Robert
Lang, Walter B.
Peterson, Floyd C.

Toledo Section

Bach, Ernest N.

University of Illinois Section

Ginsburg, Harold Marion
Mitchell, David T.

University of Michigan Section

Gordon, Wallace E.
Rowland, Kenneth H.

University of Missouri Section

Ziegler, Newell R.

Virginia Section

Bradford, J. A.
Coty, O. N.
Hudson, R. Page
Parkins, John H.
Redd, Andrew Walton, Jr.

Virginia Blue Ridge Section

Flynn, Bernard L.
Schumacher, John D.

Washington Section

Branch, Sarah W. (Miss)
Brown, Ronald F.
Fogle, E. Edgar
Kennedy, George H.
Kime, J. A.
Knowles, Howard B.
Wells, Percy A.

Western New York Section

Holland, John J.
Kern, Jean G.

Wisconsin Section

Cowley, Milford A.
Hatch, George Bates
Thomas, Ralph W.

No Section

Canessa, Julio
Cohn, Theodore
Diamond, Horace W.
Dingemanse, Elizabeth (Miss)
Elmore, A. Stanley
Elowson, Alfredo
Farrow, Mason L.
Ferdon, L. S.
Freire, Ana Rosa (Miss)
Griffiths, E. L.
Kubomi, On
Mameli, Efisio
Matheson, DeLoss H
Mendez, Rafael Pol
Neumann, M. B.
Phillips, Henry
Phillips, William
Raines, W. G.
Ruby, Glenn D.
Schwartz, Andrew, Jr.
Thompson, E. A.
Thomson, Alexander W.
Turnbull, Robert Hutchison
Wakefield, Ray B.

DECEASED

Adamson, George P., Searsport, Maine. Died Feb. 16, 1933.
Benoliel, S. D., Philadelphia, Pa. Died November 23, 1932.
Bjerregaard, August P., Weleetka, Okla. Died November 26, 1932.
Buchanan, G. H., Westfield, N. J. Died January 21, 1933.
Burdick, A. S., North Chicago, Ill. Died February 11, 1933.
Callenbach, J. A., 288 Bank St., Norfolk, Va.
Chapman, A. Chaston, London, England. Died October 17, 1932.
Clark, J. M., West Chester, Pa. Died July 15, 1932.
Clark, Merton A., Holland, Mich. Died December, 1932.
Crowe, William A., Royal Oak, Mich. Died November 23, 1932.
Elmore, Frank E., Hertsfordshire, England. Died July 26, 1932.
Erskine, Robert, Philadelphia, Pa. Died January 12, 1933.
Fujii, S., San Francisco, Calif. Died January 10, 1932.
Goldschmidt, S. A., New York City. Died January 28, 1933.
Harding, E. P., Minneapolis, Minn. Died October 10, 1932.
Hill, W. K., Carthage, Ill. Died November 20, 1932.
Hinckley, Everett H., Mamaroneck, N. Y. Died April 29, 1932.
Jones, A. Halden, Los Angeles, Calif. Died Jan. 22, 1933.
Kolle, Gotthold, Frankfurt a/Main, Germany.
Lammert, Olive M., Poughkeepsie, N. Y. Died October 9, 1932.
McKeown, R. B., Youngstown, Ohio. Died September 30, 1932.
McVeigh, Patrick F., Mt. St. Charles College, Helena, Mont. Died Feb. 20, 1933.
Morris, Fearing H., New York City. Died October 16, 1932.
Palacious, G. Delgado, Caracas, Venezuela. Died April 18, 1931.
Shiono, Chojiro, Osaka, Japan.
Skidmore, Wm. R., 806 W. Santa Fe Ave., Flagstaff, Ariz. Died Dec. 6, 1932.
Smith, Ernest R., St. Louis, Mo. Died December 30, 1932.
Smith, H. Gregg, University of Iowa, Iowa City, Iowa. Died Feb. 26, 1933.
Streeter, Leon R., Geneva, N. Y. Died December 27, 1932.
Thomas, John, Manchester, England. Died January 18, 1933.
Tucker, Thomas, London, England. Died Jan. 1, 1933.
Wood, Priscilla E., Kalamazoo, Mich.

Issued with the June Number, 1933

Proceedings

DIRECTORS' MINUTES

By call of the chairman of the board, the directors met at The Chemists' Club, New York City at 11:30 A. M., Saturday, May 13, 1933, with Charles L. Reese in the chair, and the following directors present: Robert T. Baldwin, W. D. Bigelow, E. M. Billings, A. B. Lamb, Thomas Midgley, Jr., James F. Norris, Charles L. Parsons, Walter A. Schmidt, M. C. Whitaker, F. C. Whitmore.

It was voted that hereafter the subscription rate for the *Analytical Edition* of *Industrial and Engineering Chemistry* when taken separately shall be $2.00 a year.

Communications from Mrs. Morris Loeb, which had been for some time before the directors, were then discussed, after which the following resolution, as worded by counsel, was passed unanimously:

WHEREAS, Dr. Morris Loeb, in and by Paragraph "Twelfth" of his Last Will and Testament, dated January 12th, 1912, and duly admitted to probate in the Surrogate's Court, provided:

> "I give and bequeath to the American Chemical Society, a New York corporation, the sum of twenty-five thousand dollars, to be held by it as a special fund, the income of which alone shall be used for the establishment or maintenance of a chemical type museum either in connection with The Chemists' Club of New York City or the National Museum in Washington, or the American Museum of Natural History in New York City,—preference to be given in the order in which they are named. The chief object of this museum shall be the preservation of all new substances described as the result of chemical research, either by obtaining the same by gift or purchase from the discoverer or by causing the same to be prepared in sufficient quantity according to the discoverer's published directions; all for the purpose of facilitating comparison by subsequent observers. My said executors may, in their discretion, pay this bequest or any part thereof in stocks or bonds, rated at par value of any corporation devoted to the interest of Chemistry or of Chemists, of which I may die possessed, excluding, however, any stocks of the Chemists' Building Company of which I may die possessed."

and

WHEREAS, the American Chemical Society received the bequest under said Will and set it up on its books as a special trust fund, and has duly complied with the provisions of the Will, and

WHEREAS, the income from said trust fund was used for the establishment and maintenance of a chemical type museum, first with The Chemists' Club, of 52 East 41st Street, New York City, and, upon the relinquishment by said The Chemists' Club of New York City of its control, establishment and maintenance of said chemical type museum, then with the National Museum in Washington (Smithsonian Institute), and

WHEREAS, two communications have been received from Mrs. Eda K. Loeb, the widow of Dr. Morris Loeb, both addressed to Dr. Arthur B. Lamb, President of this Society, the first dated March 23, 1933, and the second dated April 13, 1933, stating that, as the result of certain reports received by her about the National Museum in Washington, and as the result of a personal inspection of the collection a few years ago, she has arrived at the conclusion that the National Museum in Washington is not serving any very useful purpose because the fund is insufficient, and the great developments in the chemical world have outrun Dr. Loeb's intentions, and that it is her wish and thought that the fund be transferred to The Chemists' Club as a trust fund for the Club Library, and that this Society relinquish and surrender all right as trustee to hold said fund as a special fund, and

WHEREAS, this Society has been advised by counsel that by reason of the provisions of said Paragraph "Twelfth" of the Will of Dr. Loeb not only the National Museum in Washington, but the American Museum of Natural History in New York City, should relinquish any right or claim to the income from said trust fund, and

WHEREAS, There are now at the National Museum in Washington upward of 1000 specimens of various chemicals in the collection, together with records, storage cabinets and laboratory equipment, and

WHEREAS, the Society has been advised that, pursuant to Section 12 of the Personal Property Law of the State of New York, it is privileged, as the trustee holding said fund, to apply to the Supreme Court of the State of New York for an Order permitting this Society to use the income from said fund for a different purpose, or permitting the Society to transfer the principal of said fund to another or different Society, or trustee, to be administered by another or different Society or trustee, for a different and more beneficial purpose,

NOW, THEREFORE, upon due consideration by the Directors of this Society, at a meeting duly held on May 13, 1933, at which more than a majority was present, the following was unanimously

RESOLVED, that the American Chemical Society notify Mrs. Morris Loeb that it is in accord with her views and that it is willing to make application to the Supreme Court of the State of New York for an Order allowing it to resign as trustee of said fund and to turn over the same to another or different Society or trustee, to be appointed by the Supreme Court of the State of New York, and to be thereafter administered and expended as in the judgment of said Court will most effectually accomplish the general purpose of the said bequest, without regard to and free from any specific restriction, limitation or direction contained in said bequest, and also providing that Mrs. Loeb will obtain the consents and relinquishments from the American Museum of Natural History in New York City and the National Museum in Washington, and will also take such steps as may be necessary for the removal and disposal of said specimens, records, storage cabinets and laboratory equipment now in the National Museum in Washington, and that all expenses of every kind and description whatsoever in connection therewith will be borne solely by Mrs. Loeb, and that this Society shall be put to no expense whatsoever in connection therewith, and that the Society or successor trustee to be appointed by the Supreme Court of the State of New York will accept from the American Chemical Society the trust fund in such form and in such amount as it is allocated on the books of the American Chemical Society. Unanimously adopted.

The Finance Committee having submitted the statement:

> "We have now received a request from Title Guarantee & Trust Company (Mortgagor) that we submit voluntarily to a scaling of the interest from 5$^1/_2$% to 4% on the $100,000.00 mortgage certificate which includes by our own bookkeeping operation the principal of the Morris Loeb Fund. The total mortgage is $575,000.00. The mortgagor says this reduction will assist the mortgagee to meet the principal when due. The new law, of course, prevails that even with the reduction if, when and as possible, the mortgagor cannot pay us beyond the interest he receives even though it be less than 4%."

it was voted unanimously to refer the matter to the Finance Committee with power to act should they be of the opinion that the reduction should be agreed to; provided that, with the advice of counsel, they can assure themselves that all other certificate holders (sum of $475,000.00) likewise agree and that all the legal aspects have been approved by counsel.

The meeting then adjourned at 4:50 P. M. daylight saving time.

CHARLES L. PARSONS, *Secretary*

COUNCIL

MEMBERS ELECTED BETWEEN APRIL 15 AND MAY 15

AMES SECTION
Kagy, Elbert O.

CALIFORNIA SECTION
Walls, W. L.

CHICAGO SECTION
Crews, Donald L.
Faurot, Henry, Jr.
Phelps, Guy W.
Stieren, Hans George
Tenney, Robert I.

CINCINNATI SECTION
Heilig, William

CLEVELAND SECTION
Stansbury, John G.

DELAWARE SECTION
Bryant, W. M. D.

DETROIT SECTION
Stanley, George

ERIE SECTION
Rumberger, G. Glen

INDIANA SECTION
Hale, Joseph B.

KANAWHA VALLEY SECTION
Downes, Alfred W.

LOUISIANA SECTION
Belton, William Edward

NEW HAVEN SECTION
Darken, Lawrence Stamper
Kortschak, Hugo P.

NEW YORK SECTION
Garden, Nelson B.
Graff, Abner
Kirshen, Jack
Menges, Charles P.
Pribyl, Edward U.
Ruskin, Simon L.
Silleck, Clarence F.

NORTH JERSEY SECTION
Ast, George O.

NORTHEASTERN SECTION
Bunker, Kenneth M.
Killian, J. R., Jr.
Matthews, Harold
Nealand, George Edward
Noonan, Francis Joseph
Porter, Eliot F.
Sullivan, Francis M.

OKLAHOMA SECTION
Horton, Paul H.
Schmidt, Herman A.

OREGON SECTION
Grill, Frederick

PHILADELPHIA SECTION
Spitz, Albert W.
Vickers, Percy

PUGET SOUND SECTION
Hooton, A. W.
Matson, James H.

SOUTHERN CALIFORNIA SECTION
Baumbach, Harlan L.
Thomas, William J.

ST. LOUIS SECTION
Franz, Arvel
Hecker, Edgar H.
Wilbur, R. C.

UNIVERSITY OF ILLINOIS SECTION
Lehman, Milford R.
Tsao, Chien Yu

UNIVERSITY OF MICHIGAN SECTION
Friend, Leo

WASHINGTON SECTION
Bailey, Henri Lewis
Barbella, Nicholas G.
Walker, Reed

NO SECTION
Biles, J. L.
Carter, Douglas H.
Gatesman, Calvin J.
Grunwald, Oscar
Hardy, Frederick
Herman, B.
Hyma, Andrew M.
Isomura, Otomi
Joffe, Isaak S.
Kaufman, Charles Wesley
Mahmoud, Ahmed.
S. A. des Établissement
Roure Bertrand Fils &
Justin Dupont

Proceedings

GENERAL MEETING MINUTES

The Eighty-sixth General Meeting of the American Chemical Society was held in Chicago, Ill., Monday, September 11 to Friday, September 15, 1933, inclusive. A full account of the meeting will be found in the *News Edition* of *Industrial and Engineering Chemistry* for September 20 and October 10, 1933.

The Council meeting was held at 9:30 A. M., Wednesday, September 13, 1933.

On Tuesday evening a complimentary boat ride was enjoyed on Lake Michigan, where a view of the brilliantly lighted "A Century of Progress Exposition Grounds" was enjoyed.

On Wednesday afternoon four general papers, as follows, were presented before the general meeting: "Photographing the Rainbow," by C. E. K. Mees; "Cosmic Rays," by W. F. G. Swann; "Research on Metals and Alloys," by F. C. Frary; "Maleic Acid and Phthalic Anhydride," by C. R. Downs.

On Wednesday afternoon at 2:00 P. M., a general meeting of the Society was held in the Grand Ballroom of the Stevens Hotel, advance notice of the meeting having been given to vote on the proposition of amending the Certificate of Incorporation of this Society by increasing the number of Directors from thirteen (13), as at present, to fifteen (15), and to authorize the President and Secretary to make, execute, and file the necessary certificates and affidavits, showing such increase of Directors, in the proper offices where the Certificates of Incorporation of this Society have been heretofore filed.

It was moved by H. E. Howe, seconded by E. M. Billings, and unanimously passed by the assembled membership, a quorum being present, that the number of Directors of the American Chemical Society be increased from thirteen (13), the present number, to fifteen (15).

It was moved by E. J. Crane, seconded by L. V. Redman, and unanimously carried by the assembled membership, a quorum being present, that the President and Secretary of the American Chemical Society be and they are hereby authorized and directed to make, execute and file in the proper offices certificates showing the increase in number of Directors heretofore authorized, and to make, execute and acknowledge all affidavits and certificates in connection therewith, and to do all things that may be essential or necessary to effect such increase in the number of Directors, and that the Certificate of Incorporation shall be amended by showing the increase of Directors from thirteen (13), as at present, to fifteen (15).

On Wednesday evening a subscription dinner and the Willard Gibbs Award was held in the Grand Ballroom of the Stevens Hotel. The special occasion of the evening was the award of the Willard Gibbs Medal to Richard Willstätter. The dinner was followed by music and dancing.

On Thursday evening in the Great Hall, Hall of Science, at the Exposition, President Lamb gave his presidential address on the subject "A Century of Progress in Chemistry," which was followed by the presentation of the American Chemical Society Award in Pure Chemistry to F. H. Spedding. This was followed in turn by a reception to Doctors Willstätter, Karrer, Barger and Brønsted, guests of the Exposition in connection with the meeting of the American Chemical Society.

On Friday afternoon and evening there were outdoor sports on the Northwestern University campus, followed by a complimentary supper in the Northwestern University gymnasium, and an entertainment largely given by local talent in the Patten Gymnasium.

The registration showed 3191 members and guests present.

Charles L. Parsons, *Secretary*

DIRECTORS' MINUTES

The Directors of the American Chemical Society met at 9:30 A. M., Monday September 11, 1933, in the Stevens Hotel, Chicago, Ill., with Charles L. Reese in the chair and Directors Roger Adams, Robert T. Baldwin, W. D. Bigelow, Erle M. Billings, Arthur B. Lamb, Thomas Midgley, James F. Norris, Charles L. Parsons, Robert E. Wilson and Frank C. Whitmore present.

After a careful discussion of the request of the United States Trust Company of New York for advice from the American Chemical Society covering the allocation of the Herman Frasch Foundation Fund for the second period of five years beginning with January 1, 1934, the following resolutions were passed:

> "RESOLVED that in the opinion of the American Chemical Society, speaking through its Board of Directors, based on the report of its representative, Professor Roscoe W. Thatcher, satisfactory progress has been achieved during the first five-year period by all three institutions to which the Herman Frasch Foundation funds have been allocated.
>
> "RESOLVED that, while the Board of Directors appreciate the fact that the proper allocation of the reduced funds available is a difficult problem, nevertheless, in view of the provision of the will that the trustees shall 'continue to make payments for a further term of five years' unless the Society is prepared to certify that unsatisfactory progress has been made, and considering the progress to date and the future promise of the problems involved, the Board, acting for the American Chemical Society, recommends that during the second five-year period the available funds be allocated forty per cent. to the Boyce Thompson Institute for Plant Research, thirty-six per cent. to the University of Missouri, and twenty-four per cent. to the University of Wisconsin.
>
> "RESOLVED that the American Chemical Society, through its Board of Directors recommend that Dr. Roscoe W. Thatcher be continued in his present capacity for the second five-year period beginning January 1, 1934."

The Business Manager made a report covering the finances of the Society and their relation to the budget for 1933, indicating that it would not be necessary to draw upon the reserve funds of the Society in 1933 to the extent of more than $60,000 owing to extensive savings which have been made in the cost of paper, printing, and postage.

The Directors considered in detail the report of the Committee to consider the proposal of the Syracuse Section for a reduction of membership dues, as submitted to the Council on July 25, 1933, and with minor changes, approved by the Committee, recommended it for adoption to the Council.

The Directors voted to accept the plan proposed by H. E. Howe in his letter of August 5, 1933, for space and an exhibit at the Exposition of Chemical Industries, scheduled to take place at the Grand Central Palace in New York City in December, 1933, and appropriated $500.00, or such part thereof, as may be necessary to cover expenses. The Treasurer was authorized to make the necessary expenditures.

The Directors voted that the American Chemical Society Prize in Pure Chemistry be awarded in 1934, Dr. A. C. Langmuir having expressed his intention to contribute One Thousand Dollars therefor. They instructed the Secretary to express their appreciation to Dr. A. C. Langmuir for the continuation of this prize.

The Directors voted to approve in full the action of the Executive Committee as outlined in their minutes of June 17; the special meeting of the Committee of the Directors held August 9; and the minutes of the Executive Committee of August 9, 1933, covering particularly their action with reference to the contract with the Chemical Catalog Company on advertising and on monographs, and approved fully the contracts entered into and signed by the President and the Business Manager under the instructions there given.

To legalize the action covering the format and other matters tentatively settled by correspondence since the previous meetings of the Directors, and to effectuate the report of the Committee on Membership Dues, should that report be accepted by the Council and adopted by the membership, the Directors passed the following votes:

Voted, that the annual subscription rates to non-members for the Society's publications shall be as follows:

1. Chemical Abstracts	$12.00
2. Journal of the American Chemical Society	8.50
3. Industrial and Engineering Chemistry:	
a. Industrial Edition	5.00
b. News Edition	1.50
c. Analytical Edition	2.00
a and c in combination	6.00
a, b and c complete	7.50

Also, that a discount of 10% be allowed for combinations of 1, 2 and (or) 3 (complete); that members of the Society for extra subscriptions, personally addressed, be allowed a discount of 10% from these rates to the public and that the extra subscription rate to members be extended to the Chemical Society (London) and to the Netherlands Chemical Society so long as they continue similar return privileges on their publications to the members of the American Chemical Society. Non-member subscriptions may begin at any time.

Voted, that the price on back volumes of the Society's journal to members be at a discount of 20% from the following which are established as prices to the public on and after January 1, 1934, if still available:

Chemical Abstracts Vols. 1–15, inclusive	$20.00
Chemical Abstracts Vols. 16 et seq	15.00
First Decennial Index complete	40.00
Second Decennial Index complete	50.00
Journal of the American Chemical Society	9.00
Industrial and Engineering Chemistry:	
a. Industrial Edition	9.00
b. Analytical Edition	3.00
c. News Edition	2.00

Voted, that the Society both for reasons of utility and economy establish for Chemical Abstracts beginning with January 1, 1934, the standard format of $7^{7}/_{8}$ by $10^{1}/_{2}$ inches.

Voted, that the Society both for reasons of utility and economy establish for the Journal of the American Chemical Society beginning with January 1, 1934, the standard format of $7^{7}/_{8}$ by $10^{1}/_{2}$ inches.

Voted, that beginning with the January 1, 1934, journals, no free reprints be given to authors of articles appearing in the Society's publications and that the editors and Business Manager be instructed to draw up a new schedule of prices for reprints calculated to meet the cost of publication.

Voted, that the rebates now allowed local sections for securing additional members be reduced 50%.

Voted, that the expenses of the General Society heretofore charged to General Meetings be paid from any surplus remaining from registration fees after the legitimate costs of the meeting to the host local section have been met.

Voted, that, in view of the serious financial conditions to which many of our members have been subject in recent years, any member or past member of the Society now in arrears for dues may be allowed to resign in good standing by returning prepaid to Easton, Pa., any journals he may have received during January and February of the year of his first delinquency (or $3.00 in lieu thereof) and that he may then apply again for membership, without prejudice, under the membership requirement at that time existing.

Voted, that the Journal of the American Chemical Society and Chemical Abstracts shall be removed from the mailing list with the first issue for January, 1934 for all subscribers and members whose remittance, or written order for continuance, has not been received but that Industrial and Engineering Chemistry be continued through February as usual.

Voted, that all members be informed both by letter from the Secretary's office and in the News Edition that the Society does not hold itself responsible to members for furnishing to them any back numbers of the 1934 publications unless their subscriptions are placed and paid for on or before December 15, 1933. This notice is made necessary owing to the uncertainty of the number to be printed unless the Society has been given definite and advance notice of the demand.

Voted, that in case the Society is unable to furnish back numbers on any current subscription that the Business Manager be authorized to accept prior to October 1 of any year a subscription for the balance of the year at the pro rata rate plus 25%.

Voted, that the Business Manager be authorized to do all things necessary to put the new regulations, rates, and By-Laws into effect and that his budget for 1933 be increased by an amount not to exceed $3000 to enable him to do so, and the Treasurer is hereby authorized to make the necessary expenditure.

A report was presented by the Treasurer and by the Finance Committee under date of September 10, which was discussed and accepted, and the Secretary was instructed to place same on file. The report of the Finance Committee showed the following changes in securities:

> "The U. S. Treasury 3% 1955—par $25,000 costing $24,406.27 were sold for $24,140.62 (loss $265.65). This was a temporary investment and the proceeds were used for general purposes.
>
> "The U. S. Treasury 4% 1954/44—par $50,000, costing $51,432.50 were sold for $52,906.25 (profit $1473.75). This was a temporary investment and the proceeds were used for general purposes."

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*

COUNCIL MINUTES

The Council of the American Chemical Society met in the Stevens Hotel, Chicago, Illinois, at 9:30 A. M., Wednesday, September 13, 1933. with President A. B. Lamb in the chair and the following 167 councilors present:

Ex-Officio.—L. H. Baekeland, Wilder D. Bancroft, F. E. Bartell, W. D. Bigelow, E. M. Billings, J. B. Brown, E. J. Crane, H. W. Dahlberg, F. B. Dains, Edward C. Franklin, A. W. Gaugey, H. C. Hamilton, H. E. Howe, D. B. Keyes, E. W. Magruder, C. S. Marvel, Thomas Midgley, Jr., E. J. Miller, James F. Norris, W. A. Noyes, C. L. Parsons, L. V. Redman, Charles L. Reese, George D. Rosengarten, H. A. Schuette, F. W. Sullivan, Jr., Frank C. Whitmore, Robert E. Wilson.

Councilors-at-Large.—Gustavus J. Esselen, Francis C. Frary, R. A. Gortner, E. Emmet Reid, E. H. Volwiler.

Local Sections.—*Akron*, Leonard M. Freeman (subs. for G. O. Oenslager), Norman A. Shepard (subs. for John N. Street). *Alabama*, J. N. Carothers. *Ames*, F. E. Brown. *California*, James H. C. Smith (subs. for W. C. Bray), Robert E. Swain (subs. for W. H. Sloan). *Central Pennsylvania*, A. J. Currier (subs. for Walter Thomas). *Central Texas*, Henry R. Henze (subs. for J. R. Bailey). *Chicago*, Gustav Egloff, W. V. Evans, Dudley K. French, B. B. Freud, Arthur Guillaudeu, Walker M. Hinman, Paul Nicholas Leech, R. C. Newton, H. I. Schlesinger, L. F. Supple (subs. for A. E. Schaar). *Cincinnati*, W. H. McAllister (subs. for F. E. Heyroth), Oscar T. Quimby (subs. for R. H. Ferguson). *Cleveland*, H. S. Booth (subs. for O. F. Tower), C. C. Rose (subs. for E. G. Pierce). *Colorado*, Clarence M. Knudson. *Columbus*, Cecil E. Boord, Wesley G. France. *Connecticut Valley*, Emma P. Carr, C. R. Hoover. *Cornell*, T. R. Briggs. *Dayton*, C. A. Hochwalt (subs. for C. S. Adams). *Delaware*, W. H. Carothers (subs. for H. A. Lubs), Arthur L. Fox (subs. for C. M. A. Stine), E. F. Hitch (subs. for E. M. Symmes). *Detroit*, T. A. Boyd, Icie G. Macy. *East Tennessee*, C. A. Beuhler (subs. for George D. Howell). *Erie*, John L. Parsons. *Florida*, Townes R. Leigh. *Georgia*, J. Sam Guy. *Indiana*, H. A. Shonle, G. H. Shadinger. *Iowa*, George H. Coleman. *Kansas City*, James A. Austin (subs. for James E. Wildish). *Lehigh Valley*, E. F. Marsiglio (subs. for H. M. Ullmann), C. D. Pratt. *Lexington*, J. S. McHargue. *Louisiana*, C. E. Coates, Harold A. Levey. *Maryland*, Donald H. Andrews, Neil E. Gordon (subs. for F. O. Rice), Duncan MacRae (subs. for J. C. W. Frazer). *Michigan State College*, R. C. Huston (subs. for O. B. Winter). *Milwaukee*, Walter D. Kline, James W. Lawrie. *Minnesota*, C. H. Bailey. *Montana*, Oden E. Sheppard (subs. for A. E. Koenig). *New Haven*, Arthur H. Smith. *New York*, Arthur E. Hill (subs. for A. W. Hixson), C. M. Hoke (subs. for A. B. Newman), R. E. Kirk, Victor K. La Mer (subs. for C. V. Ekroth), C. S. Leonard, H. Burton Lowe, D. P. Morgan, Jr., Ralph H. Müller, R. R. Renshaw (subs. for F. E. Barrows), H. C. Sherman (subs. for Lois Woodford), Foster Dee Snell (subs. for R. P. Soule), F. M. Turner (subs. for R. M. Burns), Florence E. Wall (subs. for S. D. Swan), Lincoln T. Work (subs. for L. P. Hammett). *North Carolina*, Nevill Isbell. *Northeastern*, M. J. Ahern, George S. Forbes, Arthur D. Holmes, Harold A. Iddles (subs. for A. W. Rowe), L. A. Pratt (subs. for Stewart B. Foster), Wilhelm Segerblom, Raymond Stevens (subs. for William P. Ryan), Donald K. Tressler (subs. for Reid Hunt). *Northeast Tennessee*, C. H. Penning. *Northeast Wisconsin*, L. C. Fleck. *North Jersey*, M. L. Crossley, Harry L. Fisher, R. H. Gerke (subs. for George Maverick), Robert J. Moore (subs. for Carlton Ellis), Wm. Rieman, III (subs. for W. T. Read), John H. Schmidt, Ralph C. Shuey (subs. for L. W. Parsons). *Oklahoma*, C. G. Schmitt (subs. for C. T. Langford). *Philadelphia*, H. A. Alsentzer (subs. for H. C. Porter), C. S. Brinton (subs. for E. F. Cayo), H. A. Bruson (subs. for W. T. Taggart), J. Bennett Hill, A. G. Keller (subs. for W. R. Gerges), Martin Kilpatrick (subs. for Carl Haner), Hiram S. Lukens, Owen L. Shinn (subs. for W. J. Kelly), William Stericker. *Pittsburgh*, C. E. Brown (subs. for H. V. Churchill), Franklin P. Lasseter (subs. for L. H. Cretcher), Alexander Silverman, J. C. Warner (subs. for J. H. James), J. C. Whetzel. *Princeton*, Gregg Dougherty. *Puget Sound*, Rex J. Robinson (subs. for H. K. Benson). *Purdue*, H. B. Hass. *Rhode Island*, L. F. Foster (subs. for R. F. Chambers). *Rochester*, Florus R. Baxter (subs. for V. J. Chambers), John R. Murlin (subs. for C. J. Staud), S. E. Sheppard (subs. for H. LeB. Gray). *Rhode Island*, Laurence S. Foster (subs. for R. F. Chambers), N. W. Rakestraw. *Saint Louis*, John H. Gardner, Lyman J. Wood. *Southeast Kansas*, J. R. Sheppard (subs. for J. A. Yates). *South Jersey*, W. S. Calcott (subs. for R. E. Rose). *Syracuse*, Albert L. Elder (subs. for R. C. Roberts), J. H. Nair. *University of Illinois*, R. C. Fuson, W. H. Rodebush. *University of Missouri*, L. D. Haigh (subs. for Herman Schlundt). *Virginia*, W. Catesby Jones, L. W. Himmler (subs. for G. Ryland). *Washington, D. C.*, L. B. Broughton (subs. for R. E. Gibson), James H. Hibben (subs. for Edward Wichers), Paul E. Howe (subs. for E. W. Washburn), Henry G. Knight, H. P. Newton (subs. for H. T. Herrick), M. X. Sullivan. *Western New York*, Paul J. Carlisle, G. H. Cartledge (subs. for H. W. Post), Manley L. Ross (subs. for J. F. Williams). *Wisconsin*, Farrington Daniels, Norris F. Hall.

The names of members deceased since the spring meeting of 1933 were read to the Council and the Council stood a few moments in silent tribute to their memory.

At the request of the President, the Business Manager of the Society gave a brief statement to the Council regarding the Society's finances, which showed some improvement over the budget adopted by the Directors in December, 1932.

The Council voted that the spring meeting of 1935 be held in New York City.

It was voted that the fall meeting of the Society in 1935 be held in San Francisco.

The By-Laws of the Division of Chemical Education, approved by the Council at the Minneapolis Meeting and revised at the Chicago Meeting, were approved by the Council as follows:

BY-LAWS OF THE DIVISION OF CHEMICAL EDUCATION OF THE AMERICAN CHEMICAL SOCIETY

ARTICLE I

Name and Objects

Section 1. This Division shall be known as the Division of Chemical Education of the American Chemical Society.

Section 2. The chief object of this Division shall be to offer a common meeting ground for those interested in different branches of Chemical Education, and to coöperate with other divisions and organizations, particularly with state or regional associations of chemistry teachers.

The Division may, through special committees, conduct investigations and studies relating to any phase of chemical education.

The Division may, at its discretion, publish a journal called The Journal of Chemical Education, which shall be the official organ of the Division. The entire management of this Journal, including the appointment and replacement of the Editor, shall be in the hands of a Board of Publication, consisting of the Chairman and Secretary of the Division and three other members to be chosen by the Executive Committee for terms of three years.

ARTICLE II

Membership

Section 1. There shall be two classes of members: active and associate.

Section 2. Active membership shall be open only to members of the American Chemical Society.

Section 3. Associate membership shall be open to any person who is interested in the objects of the Division and who is not a member of the American Chemical Society.

Section 4. Associate members shall be entitled to attend the meetings of the Division and take part in the discussion of the papers only under the conditions established by the rules of the Society for non-members. They shall not have the power of voting, holding office, or reading papers before the Division. They shall have access to all committee reports and other investigations carried out by the Division but shall not be entitled to any other privileges of the American Chemical Society.

Section 5. Annual dues for active members shall be one dollar; for associate members, two dollars.

Section 6. Any person qualified under these By-Laws may become an active or an associate member of the Division by formally announcing his intention in writing to the Secretary and indicating his willingness to abide by the rules of the Division. The Secretary shall thereupon notify him of his enrollment as a member.

ARTICLE III

Officers

Section 1. The officers of the Division shall be a Chairman, a Vice-Chairman, a Secretary, a Treasurer, an Executive Committee, and the Editor of the Journal of Chemical Education.

Section 2. The Executive Committee shall consist of the other officers, the two immediate past Chairmen of the Division and one member-at-large, to be elected by ballot at the annual meeting.

Section 3. At the first session of the Division during the annual meeting of the American Chemical Society, the Chairman shall appoint from the members present at the meeting, a committee of three to nominate officers, except the Editor of the Journal of Chemical Education, for the ensuing year. At the last business meeting of the Division this committee shall present its list of nominations.

Section 4. All officers, except the Editor of the Journal of Chemical Education, shall be elected by ballot of the active members present at the last session of the Division during the annual meeting of the American Chemical Society, and shall take office at the close of the meeting at which they were elected. They shall hold office for one year or until their successors are elected, except the Secretary and Treasurer, who, if reëlected, hold office for three years.

Section 5. Vacancies in any office, except that of Editor of the Journal of Chemical Education, which may occur between meetings, shall be filled by the Executive Committee, but only for the unexpired terms.

Section 6. It shall be the duty of the Chairman to represent the Division in the Council of the American Chemical Society, to preside at the meetings of the Division and of its Executive Committee and to execute their decisions and recommendations.

Section 7. In the absence of the Chairman, his duties, except that of representing the Division in the Council, shall be performed by the Vice-Chairman.

Section 8. It shall be the duty of the Secretary to arrange the program for the meetings, to record and preserve the minutes and proceedings of the Division and of the Executive Committee, to keep a list of the active and associate members, to send members such notices as may be required, to transmit to the Secretary of the American Chemical Society the names of all officers and committees of the Division within three weeks of their election or appointment and to notify the Secretary of the American Chemical Society of any changes in officers and committees during the year.

Section 9. It shall be the duty of the Treasurer to receive all contributions and collect all dues from members, to have charge of the funds of the Division, and to make such disbursements therefrom as may be authorized by the Executive Committee and formally approved by the Chairman and Secretary.

Section 10. The Executive Committee shall manage the affairs of the Division and perform any other work delegated by the Division. Funds of the Division shall not be spent nor expense incurred by any officer or committee unless the money is appropriated or the expense authorized in advance by the Executive Committee. Requests for such appropriation or authorization must be made to the Executive Committee in time to permit necessary action.

ARTICLE IV

Meetings

Section 1. There shall be a meeting of the Division at each general meeting of the American Chemical Society. The reading of papers and discussions shall constitute the major part of the program.

Section 2. The business meetings of the Division shall come at such times as the Chairman and Secretary shall select and the order of business shall be substantially as follows:

Reading of Minutes.
Report of Secretary.
Report of Treasurer.
Report of Executive Committee.
Report of special committees and discussion.
Miscellaneous business.

ARTICLE V

Amendments

Section 1. Amendments to these By-Laws shall be made only at the annual meeting of the Division by a two-thirds vote of the active members present, provided one month's notice of the proposed amendment has been given, either by publication in the Journal of Chemical Education or in writing to the active members of the Division.

Section 2. Amendments to the By-Laws to be effective must be approved by the Council of the American Chemical Society.

Arthur B. Lamb, E. J. Crane, and H. E. Howe, were unanimously reëlected editors of the *Journal of the American Chemical Society*, *Chemical Abstracts*, and *Industrial and Engineering Chemistry*, respectively, each for a term of three years,

H. T. Clarke and R. A. Gortner were reëlected associate editors, and L. H. Adams, G. S. Whitby, and Linus Pauling were elected associate editors of the *Journal of the American Chemical Society.*

F. A. Lidbury, A. D. Little, and C. E. K. Mees were reëlected to the editorial board of Technologic Monographs.

R. A. Gortner and Farrington Daniels were elected as two of the representatives of the American Chemical Society on the board of trustees of the *Journal of Physical Chemistry.*

The chemists of Gloucester, Mass., withdrew their request for a local section to be known as the Cape Ann Section, having on conference with the Northeastern Section agreed to continue as members of that Section.

Erle M. Billings was reëlected to the Council Policy Committee for a term of three years, January, 1934, to December, 1936.

The report of the Committee to Consider the Question of Reduction of American Chemical Society Membership Dues, as proposed by the Syracuse Section, was presented by J. H. Nair, Chairman, and as adopted is printed in full in the *News Edition* of September 20, 1933.

As a matter of special record, the following change in the Constitution was unanimously approved by the Council and recommended to the membership for adoption by ballot printed in the *News Edition,* as allowed in such cases by the Constitution:

Change Section 1, Article VII, now reading:

> "The *Journal of the American Chemical Society, Chemical Abstracts,* and *Industrial and Engineering Chemistry* shall be distributed to all members not in arrears except to such members as shall have indicated in writing which of the Society publications they do not wish to receive."

so that it shall read;

> "The *Journal of the American Chemical Society, Chemical Abstracts,* and *Industrial and Engineering Chemistry* shall be made available to all members not in arrears under such conditions as the by-laws provide."

The following by-laws to effectuate the changes proposed by the Committee and approved by the Council were then adopted:

By-Law 14. Membership dues shall be ($9.00) nine dollars per year of which ($1.00) one dollar shall be for a subscription to the *News Edition,* beginning on payment of dues and continuing to the end of the calendar year. Of the dues so paid ($2.00) two dollars shall be credited to the publication costs of both the *Journal of the American Chemical Society* and of *Chemical Abstracts.*

By-Law 15. Any member shall have the right to one annual personally addressed subscription to one or more of the Society's three journals at the following rates, provided his membership dues for the year corresponding have been paid, *viz.*:

Journal of the American Chemical Society	$3.00
Industrial and Engineering Chemistry	3.00
Chemical Abstracts	6.00
Chemical Abstracts if taken with either Journal	5.50
Chemical Abstracts if taken with both Journals	5.00

If a member desires additional subscriptions they shall be available personally at 10% discount from regular subscription rates.

By-Law 17. Any person in arrears for dues for one year shall cease to be a member of the Society until all his arrears are paid, when he may be reinstated as a member by the Membership Committee.

By-Law 24. The Membership Committee may elect to full membership only reputable persons who have received an adequate collegiate training in chemistry or its equivalent and have been actively engaged in some form of chemical work for at least two years. Graduate study in chemistry and related fields may be accepted in place of part or all of the two-year period of professional activity in chemistry.

Persons engaged in chemical work who do not meet the requirements for full membership may be elected to junior membership and may continue as such until they have met the requirements of full membership. They shall be entitled to all privileges of membership except holding office.

Any regularly matriculated student, graduate or undergraduate, majoring in chemistry, may, on proper recommendation, be elected to junior membership and, so long as he retains such student status, shall be entitled to a discount of one-third of his membership dues, provided he subscribes to one or more of the Society's three Journals.

The Committee on Membership shall have power to interpret and apply these rules.

The Council voted that the Council Policy Committee be asked to consider again the whole question of registration fees with particular reference to the possibility of separating the entertainment fee from the necessary fee for overhead.

A number of conflicting codes having been proposed for controlling the activities of chemists, the Council voted that the President of the American Chemical Society appoint a committee to consider and prepare a code, if such a code should prove desirable, for submission to the proper authorities. It was also voted that the report so made should be referred to the board of directors for such action, if any, as they deem proper.

Paul Howe, on behalf of the Washington Chemical Society, local section of the American Chemical Society, presented the Society with a check for $1000 for addition to the Endowment Fund, which amount represented a part of the surplus left after paying the expenses of the spring meeting of the American Chemical Society in Washington, D. C. The check was accepted with thanks.

A unanimous vote of thanks was passed to the Chicago Section, and to the chairman and members of the local committees, whose efforts resulted in the largest and one of the most successful meetings in the history of the Society.

The Council then adjourned.

CHARLES L. PARSONS, *Secretary*

COUNCIL

MEMBERS ELECTED BETWEEN MAY 15 AND SEPTEMBER 15

AKRON SECTION

Johnston, Frederick L.

ALABAMA SECTION

Deignan, J. V.
Tidmore, J. W.

AMES SECTION

Gath, Carl Henry

CALIFORNIA SECTION

DeLaney, Colton
Emerson, George A.
Wright, Richard E.

CENTRAL PENNSYLVANIA SECTION

Messerly, Geo. H.
Wright, Calvert Charles

CENTRAL TEXAS SECTION

Adams, Leon Milton

CHICAGO SECTION

Barnett, Orville T.
Berkman, Sophia
Goss, William G.
Krause, Arthur H.
Mars, Inc.
Morey, Glen H.
Pokorney, Joseph
Stamberg, Charles J.
Stanley, George H.

CINCINNATI SECTION

Begien, John T.

CLEVELAND SECTION

Cooper Products, Inc.
Manly, Richard S.
Schmitkons, G. Edwin
Strater, Henry H.

COLUMBUS SECTION

Carson, E. L.
Griffith, Marion E.
Watt, George Willard

CONNECTICUT VALLEY SECTION

Bose, John R.
LaMar, Felix

CORNELL SECTION

Venable, Emerson

DELAWARE SECTION

Smith, Donald M.

Detroit Section

Poehlman, Carl A.
Ternstedt Mfg. Co.

Eastern New York Section

Malone, James E.
Quigley, James J.
Walker, Benj. M.

Florida Section

Barksdale, G. E.
Conrad, Paul
Holland, Frank L.
Rogers, Harry A.
Savage, Francis C.

Georgia Section

Branson, C. E.
Burrows, W. Herbert
Klima, Beverly B.

Indiana Section

Julian, Percy Lavon

Iowa Section

Benninghoff, Howard M.
Garwood, Lester J.

Kanawha Valley Section

Curtis, Henry S.

Kansas City Section

Campbell, K. P.
Newburn, Lawrence

Lehigh Valley Section

Rights, Fred L.

Lexington Section

Poynter, James W.

Maryland Section

Lippert, Arnold L.
McCoy, Paul
Westheimer, Frank H.

Michigan State College Section

Canniff, Thomas L.

Midland Section

Hess, T. Melville

Milwaukee Section

Buxbaum, E. C.
Lycan, W. H.
Pohl, William M.
Whelen, Myron S.

Minnesota Section

Schiflett, C. H.

New York Section

Cohen, Hyman R.
Cunningham, William K.
Diechmann, Gustav
Eagle, Henry Y.
Fitzgerald, Thomas B.
Hopper, Ralph T.
Johnston, William Redmond
Lee, C. O.
Lewton, Lucy Olga
MacKenzie, Wallace B.
Neumann, Henry T.
Oclassen, Charles Anthony
Ritchie, Richard John
Shields, Emmet A.
Summers, Llewellyn L. B.
Thompson, Will S.

North Carolina Section

White, Guy H., Jr.

Northeastern Section

Allyn, Arthur Cecil, Jr.
Brooke, Richard Owen
Jacobs, George Webster
Lalliberte, Albert
Langeland, Earle E.
Lannefeld, Theodore E.
Lindsay, Robert W.
Newkirk, F. F.
O'Brien, Robert A.
Proctor, Bernard E.
Rockwood, Henry
Sheehan, John F.
Taylor, Emery Folger
Vaughan, Francis Boyd

North Jersey Section

Guise, Arthur B.
Molinari, V.
Nazzaro, Rocco
Rust, John Beekman
Swackhamer, Farris S.
Wenker, Henry
Wilcox, David Henry, Jr.

Oklahoma Section

Reder, Ruth E.
Wallace, Vernon

Oregon Section

Tipka, Vernon L.

Philadelphia Section

Dannenbaum, Harry M.
Garger, John F.
Haring, Walter John
Keller, Edwin H.
Morgan, Leonard A.
Mulford, H. K.
Rubin, Nathan
Schreiber, Frederick W.
Watson, F. Arthur

Pittsburgh Section

Rader, Willis G.
Updegraff, Ellis P.
Watt, J. H.

Rochester Section

Pollock, Everett

Southeastern Texas Section

Strawn, Lynn R.

Southern California Section

Menshih, Nicholas
Silverman, Louis B.
Stone, William E.
Varon, Benj. E.

St. Louis Section

Barker, Charles C.
Kooyman, Daniel J.
Randall, Robert L.
Wood, Lewis E.
Yates, William M.

Syracuse Section

Koon, Charles
Lodder, William B.

University of Illinois Section

Herlocker, R. D.
Macnamara, F. L.
Rogier, F. J.

University of Michigan Section

Roberts, James B., Jr.
Sternberger, Helen R.
Ting, Hsu Huai

Virginia Section

Puette, Lucille A.

Virginia Blue Ridge Section

Pollak, Arthur

Washington Section

Bowles, William George
Hannan, Sister Mary Consilia
Horne, William A.

Western New York Section

Camelford, James Allan

Wichita Section

Brandt, Preston L.
Gaudet, John V.

Wisconsin Section

Kunz, Frederick
Verhoek, Frank H.

No Section

Baker, Julia McVicar
Balanyi, Dezso
Breedveld, G. J. F.
Comar, Raymond
Cooperative Superphosphate Works
Decker, Lemoyne E.
Dessauer, Hans M.
Dolgow, B. N.
Engel, Erich
Favorsky, Alexis
Harrington, John J.
Haynes, Chatten R.
Heuser, Emil
Higgins, Quentin J.
Kohn, Sara Anne
Magnin, Felix Jose
Murphy Chemical Co., Ltd.
Nicodemus, Otto
Oskerko, Alexander
Proskauer, Erich
Rajnik, Stanley L.
Scacciati, Giovanni
Simon, Jean
Subr, Josef
Tilicheev, Mstislav D.
Vukelich, Peter M.
Wintzer, Anna Caroline

DECEASED

Austin, M. M., Highland Park, Ill. Died March 10, 1933.
Bailey, Edgar H. S., Lawrence, Kansas. Died June 1, 1933.
Brinker, Harry L., Youngstown, Ohio. Died February 10, 1933.
Browne, Arthur Lee, Baltimore, Md. Died June 18, 1933.
Comar, Leon, Paris, France. Died September 6, 1932.
Comey, Arthur M., Cambridge, Mass. Died April 6, 1933.
Cuming, William Fehon, Melbourne, Australia. Died March 19, 1933.
Dailey, James Glanding, Toledo, Ohio. Died October 2, 1932.
Estill, Howard W., San Francisco, Calif. Died February 1, 1933.
Gifford, Geo. B., New York, N. Y. Died February 27, 1933.
Gudeman, Edward, Chicago, Ill. Died May 2, 1933.
Henriksen, Alfred, Ponca City, Okla. Died September 5, 1933.
Iversen, Morton, Brooklyn, N. Y.
King, Elmer H., New York, N. Y. Died March 15, 1933.
Lynn, George, Wadsworth, Ohio. Died July 15, 1933.
Malcolm, J. L., Natal, South Africa. Died October, 1932.
Marchand, Alfred Edgar, Norwich, Conn. Died February 21, 1933.
Miller, Sylvester, Aurora, Ill. Died April 25, 1933.
Morris, Frank H., Buffalo, N. Y.
Ortved, Niels C., Detroit, Mich. Died April 5, 1933.
Palmer, Ernest, Cle Elum, Wash. Died April 23, 1933.
Ryan, William P., Cambridge, Mass. Died June 1, 1933.
Schupphaus, Robert C., New York, N. Y. Died October, 1932.
Soars, C. Austin, Kansas City, Mo.
Ward, Fred W., Toronto, Ont., Canada. Died June 25, 1933.
Watson, Percy, Shirley, Mass. Died April 24, 1933.
Zook, Paul Ash, Passaic, N. J. Died July 10, 1933.

Issued with the December Number, 1933

Proceedings

COUNCIL

Under date of September 18, 1933, and as printed in the NEWS EDITION of INDUSTRIAL AND ENGINEERING CHEMISTRY for September 20, 1933, the membership was asked to vote on the following change in the Constitution:

Change Section 1, Article VII, now reading:

> "*The Journal of the American Chemical Society, Chemical Abstracts*, and *Industrial and Engineering Chemistry* shall be distributed to all members not in arrears, except to such members as shall have indicated in writing which of the Society publications they do not wish to receive."

so that it shall read:

> "*The Journal of the American Chemical Society, Chemical Abstracts*, and *Industrial and Engineering Chemistry* shall be made available to all members not in arrears under such conditions as the By-Laws provide."

The ballots were counted on October 17, 1933, by a committee consisting of W. D. Bigelow, H. C. Fuller and Charles L. Parsons with the following result:

In favor of the change	7586
Opposed	428

The change was accordingly adopted.

Pursuant to the vote of the Council at its meeting in Chicago, Ill., on September 13, 1933, President Lamb has appointed the following as the Committee to Consider and Report on the Need of a Code for Chemists: Carl S. Miner, Chairman, R. T. Baldwin, G. J. Esselen, H. G. Knight and J. M. Weiss.

MEMBERS ELECTED BETWEEN SEPTEMBER 15 AND NOVEMBER 15

CALIFORNIA SECTION
Wackwitz, E. F.

CHICAGO SECTION
American Maize Products Co.
Forrester, Jay H.
Heyl, G. V. F. W.
Robinson, Herbert E.

GEORGIA SECTION
Gallent, John B.

LEHIGH VALLEY SECTION
Kleckner, Lewis Joseph

LOUISIANA SECTION
Bludworth, J. E.
Seibert, Arthur H.

NEW HAVEN SECTION
Irmina, Sister M.

NEW YORK SECTION
Kellog, Henry B.
Roos, William Cornelius

NORTH JERSEY SECTION
O'Keeffe, Andrew E.

PHILADELPHIA SECTION
Peters, Allen F.

PITTSBURGH SECTION
Berl, Ernst

PUGET SOUND SECTION
Van Winkle, Marion

ROCHESTER SECTION
Foster, Richard F.

SACRAMENTO SECTION
Browning, George L.

ST. LOUIS SECTION
Wilkinson, John W.

UNIVERSITY OF ILLINOIS SECTION
Cameron, Hugh J.

WASHINGTON SECTION
McGee, Kenneth C.

NO SECTION
Bowlen, Elmer T.
Porlezza, Camillo
Potter, Earl F.
Societe Anonyme Carburanti Italia

DECEASED

Bergholtz, Edgar A., New York, N. Y.
Black, Otis Fisher, Washington, D. C. Died October 14, 1933.
Brown, Quintus, Mineral Point, Wis. Died April 22, 1933.
Cram, Marshall P., Brunswick, Me. Died October 10, 1933.
Drummond, I. W., New York, N. Y.
Edwards, W. F., Hoboken, N. J.
Fuchs, Francis J., Woodhaven, L. I., N. Y. Died June 23, 1933.
Garland, Clarence E., Morgantown, W. Va.
Hofmann, Harry E., Scotch Plains, N. J. Died May, 1933.
Jessel, Henry R., Wauwatosa, Wis. Died October 15, 1933.
Mahony, Marie M., Washington, D. C. Died June, 1933.
Millwood, James P., Passaic, N. J. Died September 24, 1933.
O'Neill, Edmond, Berkeley, Cal.
Randolph, Thorne Fitz, Danville, Ind. Died October 22, 1933.
Sacasa, Ferdinand J., Bombay, British India.
Smith, Acheson, Greenwich, Conn. Died July 7, 1933.
Sommer, Adolph, Boston, Mass. Died October 20, 1933.

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